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TETRACHLORGALLEIN AND SOME OF ITS DERIVATIVES

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[SECOND PAPER[1]]

In the first paper it was stated that the crude tetrachlorgallein was completely soluble in acetone.[2] It was thought, therefore, that it might be possible to use acetone for the purpose of purifying this product. The method was first tried on some tetrachlorgallein which had crystallized out of 94 per cent. ethyl alcohol on long standing. This material,[3] which had a light yellowish gray color, was dissolved in freshly distilled acetone, the solution concentrated by distillation and allowed to stand overnight. The next day it was found that almost colorless crystals had separated from the red solution. These were filtered off on a Buchner funnel, washed with acetone, thoroughly drained and then ground in an agate mortar until they had only a faint odor of acetone. A portion was placed in a vacuum desiccator over phosphorus pentoxide and the desiccator evacuated. The product, which was almost white at first and well crystallized, became pink and then red, while the loss of weight was considerable. Another portion of the white crystals from acetone, when allowed

[1] See THIS JOURNAL, **42**, 183 (1909) for the first paper.

[2] THIS JOURNAL, **42**, 208.

[3] This material was probably the *colorless* hydrate, see page 26.

to stand in the air, became deep red. The same color is produced more rapidly by adding water to the crystals.

Both the colorless crystals and the red product obtained from them gave the characteristic reactions of tetrachlorgallein, dissolving in dilute sodium carbonate solution with a red color and in excess of sodium hydroxide with a blue color. Both products dissolve in alcohol or acetone with a pink color which turns red on the addition of water.

A marked difference between the colorless crystals and the red product is the fact that the crystals are fairly soluble in ether while the red compound is practically insoluble in this solvent.

A small portion of the colorless crystals was placed in a platinum boat and heated to 110° in a current of carbon dioxide in the apparatus elsewhere described.[1] The outflowing carbon dioxide was passed through Hugershoff gas wash bottles containing distilled water. The water was then found to contain acetone, as shown by its odor, by the formation of large amounts of iodoform on treatment with ammonium hydroxide and iodine-potassium iodide solution, and finally by the formation of acetone phenylhydrazone on treatment with phenylhydrazine hydrochloride and sodium acetate. The substance in the boat came to constant weight after seven hours' heating at 110° and there was no further loss on heating for one hour at 156°. The loss of weight was 18.90 per cent. and the fact that no moisture condensed on the cold part of the tube indicated that this loss was due entirely to acetone, past experience having shown that even 0.5 per cent. of water in a compound leads to the deposition of moisture on this part of the tube. This loss of weight agrees closely with that required by the formula $C_{20}H_8O_7Cl_4 \cdot 2CH_3COCH_3$ for which the calculated loss (acetone) is 18.79 per cent.[2] The chlorine content of the original white crystals is also in accord with the above formula:

Calculated for $C_{20}H_8O_7Cl_4 \cdot 2CH_3COCH_3$	Found	
Chlorine	Chlorine	
Per cent.	Per cent.	
	I	II
22.95	22.83	22.75[3]

[1] THIS JOURNAL, **41**, 403.

[2] International Atomic Weights for 1911 have been used in all calculations.

[3] All chlorine determinations were made by the method described in THIS JOURNAL, **41**, 393.

The colorless crystals become intensely red when kept *in vacuo* over phosphorus pentoxide for several days. The loss of acetone is gradual and continuous, however, and no tendency to remain at constant weight was noted although the substance was kept *in vacuo* for over 75 days. It should be mentioned that the red color was most intense when the loss in weight corresponded with that calculated for *one* molecule of acetone. From this point the color became fainter until finally the compound had very little color.

Further work on these colorless crystals showed the correctness of the above formula and hence we shall call the compound

Tetrachlorgallein Diacetonate

In making the second lot of this compound, we used the *crude* tetrachlorgallein, thoroughly washed first with dilute hydrochloric acid, then with water, and air-dried at room temperature. Fifty grams of this material were dissolved in freshly distilled acetone which had been previously dried over calcium chloride, and the solution filtered and concentrated. On standing, a yellowish white crystalline compound separated. This was filtered off and crystallized *three* times from *dry* acetone. It was thus obtained as an almost colorless, beautifully crystallized product. It was filtered off with suction on a Buchner funnel and transferred to a porcelain dish, thoroughly mixed with pure acetone and again filtered. This treatment was then repeated and the product drained as dry as possible on the Buchner funnel. This material, which was practically white, was placed in a desiccator and the air pumped out as quickly as possible. Fresh air was then admitted, the material stirred thoroughly and the desiccator again evacuated. This process was repeated eight times, after which the material had no odor of acetone, but was still crystalline and almost white, having only the faintest pink tinge. It was transferred to a tightly-stoppered bottle and kept in a cool place. Some of this substance was first heated to 110° in a current of carbon dioxide in the apparatus described.[1] It came to almost constant weight after eleven hours

[1] THIS JOURNAL, **41**, 403.

and much acetone was evolved but no water. The temperature in the apparatus was then raised to 157° and the substance came to constant weight in four hours, the results being as follows:

Substance Gram	Loss at 110° Gram	Loss at 110° Per cent.	Loss at 157° Gram	Acetone Per cent.
0.4090	0.0765	18.70	0.0768	18.78
0.4643	0.0867	18.67	0.0869	18.72
	Calculated for $C_{20}H_8O_7Cl_4.2CH_3COCH_3$			18.79

The product heated to 157° had a faint pink color and was anhydrous tetrachlorgallein, as shown by the following chlorine determinations:

Substance Gram	Tenth-normal silver nitrate cc.	Chlorine Per cent.
0.3090	24.50	28.12
0.1914	15.13	28.03
	Calculated for $C_{20}H_8O_7Cl_4$	28.26

In order to determine whether these low results were due to loss of chlorine or hydrochloric acid at 157°, two more determinations were made, this time on the original substance. Although this material had been kept in a cool place, it seemed to be losing acetone. Hence the loss on heating was again determined and found to be 18.25, 18.34, 18.23 and 18.32 per cent.: mean, 18.28 per cent. Taking this mean as the acetone content, the original substance was analyzed for chlorine by both the gravimetric and volumetric methods, calculating the chlorine for tetrachlorgallein:

	Substance Gram	Tetrachlorgallein Gram	Tenth-normal silver nitrate cc.	Chlorine Per cent.	Silver chloride Gram	Chlorine Per cent.
I	0.3134	0.2561	20.25	28.04	0.2904	28.05
II	0.3400	0.2778	21.96	28.03	0.3139	27.95
			Calculated for $C_{20}H_8O_7Cl_4$			28.26

These results agree very closely with those obtained on the material heated to 157° and prove that the substance loses neither chlorine nor hydrochloric acid at this temperature. Later, after we had discovered the modification of tetrachlor-

gallein which we have called the carbinolcarboxylic acid[1] and which contains only 27.28 per cent. of chlorine, we concluded that these low results on chlorine were due to the presence of a very small amount of this carbinolcarboxylic acid in the diacetonate. The formation of this carbinolcarboxylic acid was doubtless due to the condensation of moisture on the diacetonate when its temperature was lowered by the rapid evaporation of the mechanically held acetone.[2]

The third lot of diacetonate was made from the same crude tetrachlorgallein as the first two, but the product had already been crystallized once from acetone. Twenty grams of this material were dissolved in 500 cc. of boiling acetone which had been previously carefully dried. The solution, which was claret-red, was filtered, concentrated to 300 cc., chilled rapidly and stirred occasionally. The white crystalline product which separated after a few minutes was filtered off with suction, washed with anhydrous acetone and dried in the same manner and with the same precautions used in making the second lot of the diacetonate[3], the object being to obtain the compound as free as possible from acetone held mechanically. This product, which was practically white, having only a suggestion of a faint pink tinge, was immediately bottled and analyzed.

Substance Gram	Loss at 157° Gram	Acetone Per cent.
0.4606	0.0868	18.85
0.5014	0.0945	18.85
Calculated for $C_{20}H_8O_7Cl_4.2CH_3COCH_3$		18.79

The chlorine determinations were made on the product heated to constant weight at 157° in carbon dioxide. This compound had only a slight pink tinge and is anhydrous tetrachlorgallein.

Substance Gram	Tenth-normal silver nitrate cc.	Chlorine Per cent.
0.2975	23.56	28.08
0.2700	21.47	28.20
	Calculated for $C_{20}H_8O_7Cl_4$	28.26

[1] See page 37.
[2] Page 3.
[3] Page 3.

From the close agreement of all the results, we were convinced that the diacetonate is a definite compound. Tetrachlorphthalic acid itself crystallizes with two molecules of acetone[1] and a tetrachlorgallein hydrochloride containing acetone has also been prepared.[2] It was therefore thought necessary to determine the amount of acetone in the diacetonate, in other words, to show that the loss of weight on heating to 157° was due entirely to loss of acetone. After experimenting with various methods for determining acetone, we finally adopted that of Messinger[3] as modified by Collischonn.[4] The procedure is as follows: The acetone solution is made up to about 250 cc. and 20 cc. of normal sodium hydroxide added. Tenth-normal iodine solution is then run in from a burette, drop by drop with constant shaking, until about 20 per cent. excess is present. The flask is then closed with a stopper, shaken for four minutes and acidified with five cc. of 6-normal hydrochloric acid. A measured excess of tenth-normal sodium thiosulphate solution and four cc. of starch solution (one gram of arrowroot starch in 500 cc. of boiling water) are added and the excess of thiosulphate titrated. The thiosulphate solution was standardized with pure iodine and the iodine solution was titrated against the thiosulphate under exactly the conditions given above except that no acetone was used. Acetone has a molecular weight of 58.048 and is equivalent to six atoms of iodine. Hence, each cc. of tenth-normal iodine solution is equivalent to 0.0009675 gram of acetone. The method was first tested with pure acetone. About 60 cc. of distilled water in an Erlenmeyer flask covered with a watch-glass were carefully weighed, a little more than one cc. of acetone (from the bisulphite compound, Kahlbaum's) added and the flask containing the solution weighed at once. The increase in weight was 1.148 grams, which represents the amount of acetone in the solution. This solution was then diluted to one liter and measured portions analyzed with the following results:

[1] THIS JOURNAL, **41**, 410.

[2] THIS JOURNAL, **42**, 212. Heller and Langkopf have also made a "Salzsaures Galleinacetonat." *Z. Farb. Ind.*, **5**, 267.

[3] Ber. d. chem. Ges., **21**, 3366 (1888).

[4] Z. anal. Chem., **29**, 562 (1890).

Acetone solution used cc.	Tenth-normal iodine cc.	Acetone Grams per liter
20.49	24.17	1.141
15.06	17.86	1.147
17.35	20.36	1.135
15.99	18.99	1.149
	Acetone actually present	1.148

The determination of the acetone in the tetrachlorgallein diacetonate was carried out as follows: About 0.6 gram of the substance in a platinum boat was weighed in a glass-stoppered weighing tube. The boat was then placed in the apparatus already described[1] and two Hugershoff gas wash bottles attached. These were filled with distilled water and packed in ice. The substance in the boat was then heated for one hour at 157° while a slow current of carbon dioxide was passed over the compound to drive out the acetone. The contents of the first wash bottle were then transferred to a 500 cc. measuring flask, the bottle thoroughly washed out with distilled water, the washings added to the measuring flask and the solution finally made up to 500 cc. Fifty cc. portions were titrated and the mean of three determinations was taken. The contents of the second wash bottle were also titrated, giving a slight addition. The boat with its contents was weighed again after the heating and the loss of weight determined. The results obtained were as follows:

	Substance Gram	Loss at 157° Gram	Acetone Per cent.
I	0.5814	0.1088	18.71
II	0.6625	0.1244	18.78
	Calculated for $C_{20}H_8O_7Cl_4.2CH_3COCH_3$		18.79

The solution in the first Hugershoff bottle was made up to 500 cc. and three 50 cc. portions titrated, (*a*), (*b*) and (*c*):

		Tenth-normal iodine solution		
		First bottle cc.	Second bottle cc.	Acetone Per cent.
I	(*a*)	11.24	0.55	18.80
	(*b*)	11.19	0.55	18.71
	(*c*)	11.22	0.55	18.75
			Mean	18.75

[1] THIS JOURNAL, **41**, 403.

		Tenth-normal iodine solution: First bottle cc.	Second bottle cc.	Acetone Per cent.
II	(*a*)	12.84	0.41	18.81
	(*b*)	12.82	0.41	18.78
	(*c*)	12.88	0.41	18.87
			Mean	18.82
	Calculated for $C_{20}H_8O_7Cl_4.2CH_3COCH_3$			18.79

Hence the loss of weight at 157° is due entirely to loss of acetone and the compound is properly called tetrachlorgallein diacetonate.

The process of preparing the diacetonate has been described in some detail because a number of later attempts to make this substance from the crude tetrachlorgallein, as well as from the anhydrous product, resulted in failure. Mr. T. R. Briggs found that the diacetonate can readily be obtained from the light-colored tetrachlorgallein hydrate which crystallizes out of methyl alcohol.[1] Analyses of this product made by Mr. Briggs show that it is the colorless hydrate containing a small amount of the red hydrate:[2]

Substance Gram	Loss at 158° Gram	Water Per cent.
0.2821	0.0107	3.79
	Calculated for $C_{20}H_8O_7Cl_4.H_2O$	3.47

Substance (dry) Gram	Tenth-normal silver nitrate cc.	Chlorine Per cent.
0.2714	21.59	28.21
	Calculated for $C_{20}H_8O_7Cl_4$	28.26

About 20 grams of this mixture of hydrates were dissolved in 500 cc. of redistilled anhydrou acestone, and the solution filtered and concentrated by distillation to 100-150 cc., when crystals began to separate. These were filtered off, washed with acetone and recrystallized from anhydrous acetone. The crystals thus obtained, which were almost pure white, lost acetone on standing in the air, and took up water, forming the

[1] THIS JOURNAL, **42**, 210.

[2] See pages 24 and 26.

red hydrate. Analyses, by Mr. Briggs, of the white crystals gave the following results:

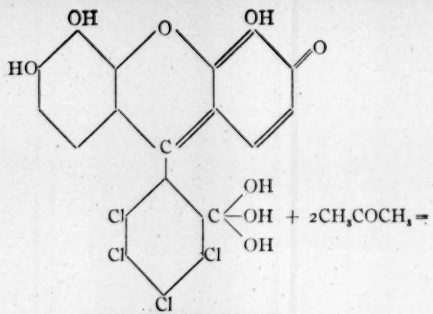
Substance Gram	Loss at 158° Gram	Acetone Per cent.
0.3956	0.0738	18.66
Calculated for $C_{20}H_8O_7Cl_4.2CH_3COCH_3$		18.79

Substance (heated to 158°) Gram	Tenth-normal silver nitrate cc.	Chlorine Per cent.
0.3218	25.50	28.10
Calculated for $C_{20}H_8O_7Cl_4$		28.26

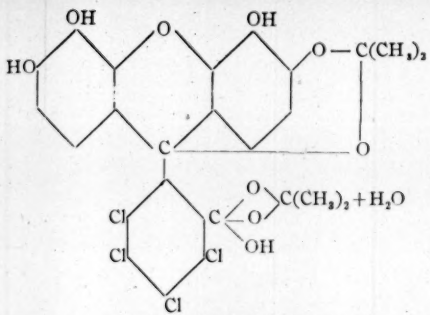
In order to observe the conduct of the diacetonate on standing in the air, a weighed amount of the substance was spread out on a watch-glass and protected from dust. Weighings were made at intervals until constant weight was reached, 64 days being required. The actual loss was 14.48 per cent. The resulting product retained the crystalline form of the colorless diacetonate but had a red color. A portion of this colored substance was then heated to 157° until it came to constant weight. The loss was 4.41 per cent., of which 0.62 per cent. was due to loss of acetone,[1] and 3.79 per cent. to loss of water. Furthermore, the substance, after being heated to 157°, weighed 0.6 per cent. more than the calculated weight of the tetrachlorgallein in the original diacetonate, proving the formation of some of the carbinolcarboxylic acid described below.[2] Hence the diacetonate gradually loses most of its acetone in the air, taking up somewhat more than one molecule of water to form the colored tetrachlorgallein hydrate and a small quantity of the colorless tetrachlorgalleincarbinolcarboxylic acid.

The formation of the diacetonate may be represented as follows:

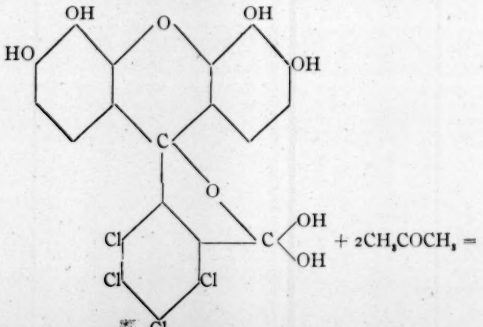
[1] Determined as in the case of the diacetonate; see page 7.
[2] Page 37.



Tetrachlorgallein Hydrate
(colored)

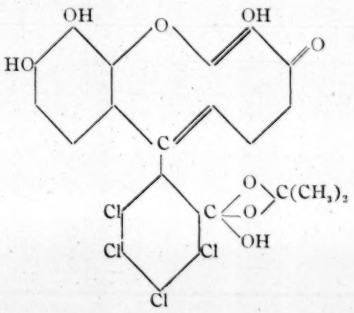


Tetrachlorgallein Diacetonate
(colorless)



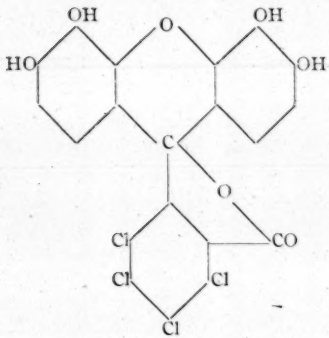
Tetrachlorgallein Hydrate
(colorless)

This formula for the diacetonate is in accord with all the facts known. It represents the compound as a colorless substance and if we suppose that the first molecule of acetone it loses is the one which joins the quinoid grouping, the resulting product would be



This has the quinoid structure and would be *colored*. It will be remembered that the colorless diacetonate gradually loses acetone and becomes *colored* when placed in a desiccator over phosphorus pentoxide and that the color is *deepest red* when the diacetonate has lost *one* molecule of acetone. From this point the color becomes fainter and the product which results from heating the diacetonate to 157° and which no longer contains any acetone has almost no color.[1] It is probably the lactoid form of tetrachlorgallein:

[1] The same product results when the colorless or the colored hydrate is heated to 157°.

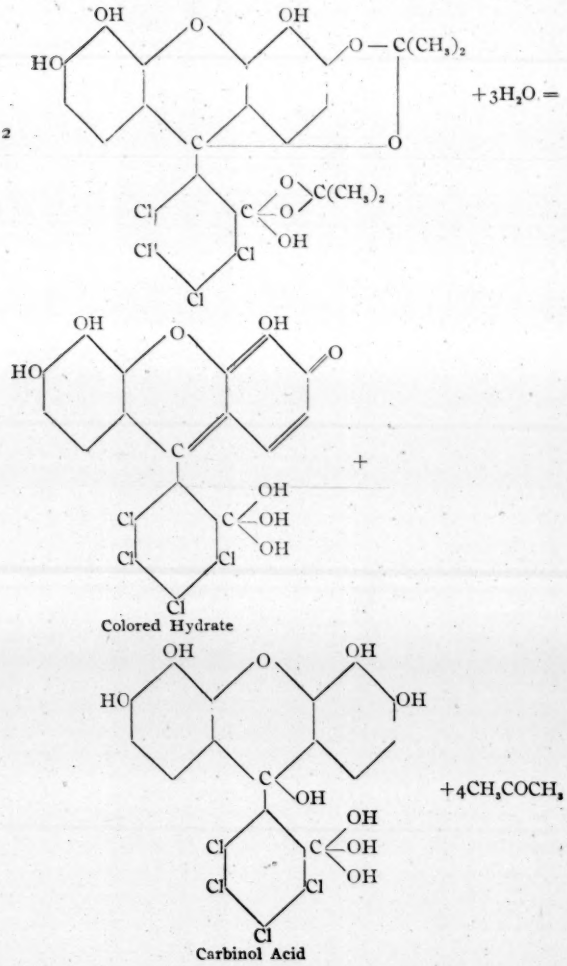


Tetrachlorgallein (anhydrous)

In this connection it may be well to call attention to the fact that the diacetonate of tetrachlorphthalic acid loses acetone when a current of air dried with calcium chloride is passed over it and the product left is the *anhydrous* tetrachlorphthalic acid.[1] On standing in the air or on boiling with water, this diacetonate loses all of its acetone and takes up a half-molecule of water, forming tetrachlorphthalic acid, $C_6Cl_4(COOH)_2 . 0.5H_2O$.[2]

The diacetonate of tetrachlorgallein takes up water when exposed to the air and forms the *colored* hydrate and a small amount of the carbinol acid:

[2] THIS JOURNAL, **41**, 410.
[2] *Ibid.*, **41**, 411.


OH
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O — C(CH3)2
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Colored Hydrate
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+4CH3COCH3
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C
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Carbinol Acid

It is probable that here, too, the first molecule of acetone lost is the one connected with the quinoid grouping. This explains in a very satisfactory manner why, when the second molecule of acetone is replaced by water, the main product of the reaction is the *colored* hydrate.

Tetrachlorgallein Etherate

Twenty grams of the pure tetrachlorgallein diacetonate were shaken vigorously for two minutes with 300 cc. of anhydrous ether, which had been previously dried with phosphorus pentoxide and distilled. The greater part of the substance dissolved, forming a reddish solution. This was filtered at once through a folded filter and the filtrate, which was perfectly clear, allowed to stand in a stoppered flask. Within two minutes a perfectly white, beautifully crystalline precipitate began to separate and in the course of fifteen minutes about 15 grams of the material had accumulated. The mixture was allowed to stand overnight at room temperature in the tightly-stoppered flask, and the crystals filtered off the next day, washed thoroughly with anhydrous ether and stirred in a crystallizing dish until the ether held mechanically by the crystals had entirely evaporated. They were then placed in a bottle, tightly corked and kept in the ice box. A weighed portion was heated to 100° for half an hour in a stream of carbon dioxide. There was no condensation of moisture on the cold part of the tube (*F*) such as is always noted when compounds containing water are heated in the apparatus,[1] but the odor of ether was very marked and persisted to the end of the heating. The loss in weight of the compound at this temperature was 9.7 per cent. The outflowing carbon dioxide was passed through Hugershoff gas wash bottles containing distilled water to remove any acetone which might have been present in the gas. The water, however, gave only an extremely minute quantity of iodoform when tested for acetone and a quantitative determination of the amount present, carried out by the method described under tetrachlorgallein diacetonate,[2] gave only 0.034 per cent., an amount so small

[1] See THIS JOURNAL, **41**, 404.

[2] See page 7.

as to be entirely negligible. The substance had acquired a faint pink color after the half-hour's heating to 100° and further heating to 157° for an hour and a half did not increase this color, though the total loss of weight at this temperature amounted to 10.4 per cent. A second lot of the etherate was made, using the same quantity of the diacetonate and the same precautions detailed above, only the product was simply stirred in the crystallizing dish until it showed no further tendency to form lumps. It was then bottled and analyzed. The following are the results obtained on the two products:

	Substance Gram	Loss at 157° Gram	Ether Per cent.
I	0.5766	0.0602	10.4
II	0.8529	0.0970	11.4
	Calculated for $C_{20}H_8O_7Cl_4.C_4H_{10}O$		12.9

The compound loses its ether very rapidly indeed and for this reason cannot be weighed in an open dish. The results, however, show that it contains approximately one molecule of ether.

A chlorine determination was made on the product obtained by heating the etherate to 157°.

Substance (heated to 157°) Gram	Tenth-normal silver nitrate cc.	Chlorine Per cent.
0.2594	20.30	27.75
Calculated for a mixture of equal parts of the anhydrous tetrachlorgallein and the carbinolcarboxylic acid		27.77

It is evident from this result that the compound heated to 157° is a mixture of the anhydrous tetrachlorgallein, which contains 28.26 per cent. chlorine, and the carbinolcarboxylic acid[1] containing 27.28 per cent. The formation of the latter is presumably due to the condensation of moisture on the compound cooled by the rapid evaporation of the ether. It will be remembered that the diacetonate also gave low results for chlorine due to the same cause.[2]

About three grams of the same etherate (II), which lost

[1] See page 37.
[2] See page 4.

11.4 per cent. in weight when heated to 157°, turned pink when exposed to the air and came to constant weight after six days with a loss of only 7.2 per cent. There was no further loss of weight, although the product stood in the air for two months after this. Hence it seems probable that all the ether had evaporated and that the difference, 4.2 per cent., between the two losses in weight (11.4 — 7.2) is due to absorption of water to form a mixture of hydrate and carbinol acid, as in the case of the diacetonate.[1] While the product from the latter, however, is *red*, that from the etherate has only a faint pink tinge. This difference is due to the fact that the diacetonate combines with water to form the *colored* hydrate and a small amount of the carbinol acid while the etherate gives the *colorless* hydrate[2] and the carbinol acid mixed with sufficient of the *colored* hydrate to produce the faint pink color.

Analyses[3] of this etherate (II), which had stood in a museum bottle for over a year, gave the following results:

Substance Gram	Loss at 157° Gram	Water Per cent.
0.2539	0.0099	3.90
0.2612	0.0098	3.75
0.2677	0.0103	3.85
	Calculated for $C_{20}H_8O_7Cl_4.H_2O$	3.47

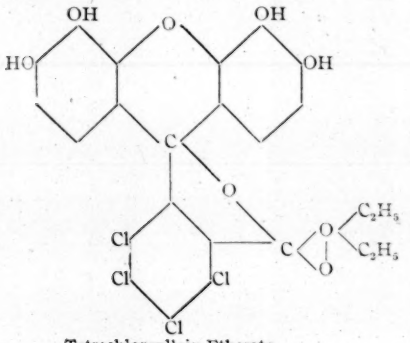
Substance (dry) Gram	Tenth-normal silver nitrate cc.	Chlorine Per cent.
0.2440	19.20	27.90
0.2514	19.75	27.86
0.2574	20.21	27.85
Calculated for a mixture of equal parts of anhydrous tetrachlorgallein and the carbinolcarboxylic acid		27.77

As the etherate is a colorless compound and is formed from the colorless diacetonate, it probably has the lactoid structure, like the anhydrous tetrachlorgallein resulting from heating the diacetonate to 157°. The ether must be represented as very loosely combined since it is so readily given off. The following structural formula is suggested for the compound:

[1] See page 9.

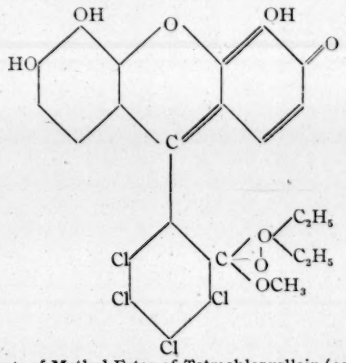
[2] See page 26.

[3] These analyses were made by Mr. T. R. Briggs.



Tetrachlorgallein Etherate

That the ether attaches itself to the carbonyl group of the phthalic acid residue and not to the quinoid grouping seems very likely, first, from the fact that the etherate loses ether and takes up water, when exposed to the air, to form a mixture of the *colorless* hydrate and the carbinol acid[1] and, secondly, from the fact that the methyl ester of tetrachlorgallein forms a *colored* etherate[2] which must have the following formula:



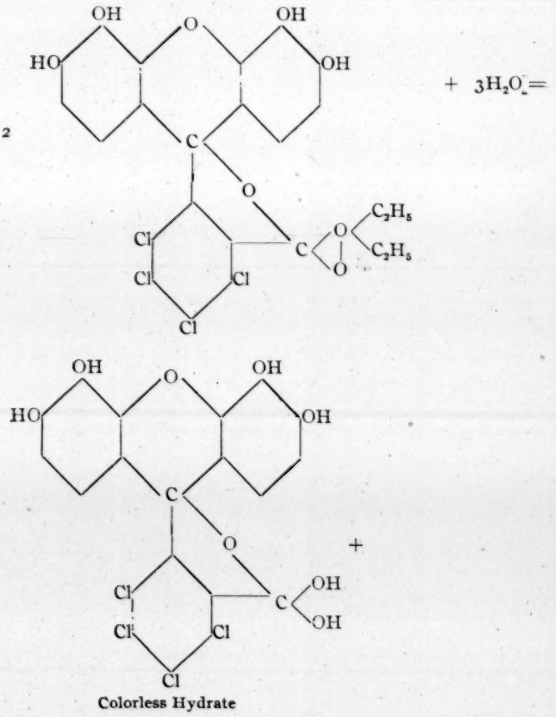
Etherate of Methyl Ester of Tetrachlorgallein (colored)

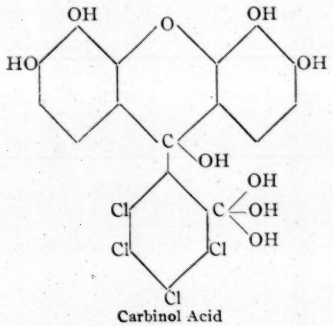
[1] See page 37.

[2] THIS JOURNAL, **42**, 237.

Hence the ether must attach itself to the carbonyl group in the phthalic acid residue and not to the quinoid grouping, otherwise this etherate would be *colorless*.

Tetrachlorgallein etherate loses ether and takes up water when exposed to the air, forming a mixture of the *colorless* hydrate and the carbinol acid:





Carbinol Acid

Tetrachlorgallein Hydrochloride[1]

It has been shown that the hydrochloride of tetrachlorgallein can be readily made by passing dry hydrochloric acid gas into a concentrated solution of tetrachlorgallein in dry acetone. The product thus obtained, however, contains acetone and it was found to be impossible to accurately determine the amount, probably owing to the action of the hydrochloric acid on the acetone. The anhydrous tetrachlorgallein, made by heating the pure diacetonate to 157° for the purpose of determining the amount of acetone it contained,[2] was found to take up dry hydrochloric acid gas very readily, becoming first red, then dark red and finally green. This green color, which was also observed in the case of the hydrochloride containing acetone, is a surface color, as the powdered material is red. The method of preparing the hydrochloride was as follows: A weighed amount of the anhydrous tetrachlorgallein in a boat was placed in a glass tube and hydrochloric acid gas, dried first with 99 per cent. sulphuric acid and then with phosphorus pentoxide, was passed over it for several hours. The boat containing the hydrochloride was then removed and weighed in a tightly-stoppered weighing tube. This process was repeated until the substance came

[1] THIS JOURNAL, **42**, 212.

[2] See page 5.

to constant weight, which required about sixteen hours' exposure. The amount of hydrochloric acid absorbed by the tetrachlorgallein is then given directly by the increase in weight.

Experiment	Tetrachlorgallein Gram	Time exposed Hours	Gain in weight Gram	Hydrochloric acid Per cent.
I	0.4412	20	0.0326	6.88
II	0.4809	20	0.0352	6.82
III	0.4752	16	0.0351	6.88
IV	0.5838	16	0.0436	6.94
V	0.4752	18	0.0350	6.86
VI	0.4286	72	0.0320	6.95
	Calculated for $C_{20}H_8O_7Cl_4.HCl$			6.77

In order to determine whether the increase of weight was due entirely to the addition of hydrochloric acid, the tetrachlorgallein hydrochloride obtained in Experiments III and IV was placed in a tube and heated to 157° in a stream of carbon dioxide which was afterward passed through two Hugershoff gas wash bottles containing distilled water. The hydrochloric acid in this water was then determined by titration, with the following results:

	Tetrachlorgallein hydrochloride Gram	Tenth-normal potassium hydroxide cc.	Hydrochloric acid Per cent.
III*a*	0.5103	9.54	6.82
IV*a*	0.6274	11.65	6.77
	Calculated for $C_{20}H_8O_7Cl_4.HCl$		6.77

The material left in the boat was anhydrous tetrachlorgallein, its weight in both cases being exactly the same as that of the original tetrachlorgallein used in preparing the hydrochloride. Indeed, the anhydrous tetrachlorgallein used in Experiment V was actually that obtained in III*a* by heating the hydrochloride to 157° to drive off the hydrochloric acid. These results show that anhydrous tetrachlorgallein is converted by the action of dry hydrochloric acid gas into tetrachlorgallein hydrochloride which, when heated to 157°, loses hydrochloric acid quantitatively with the formation of the original tetrachlorgallein. The hydrochloride is also decomposed quantitatively by hot water with the formation of

hydrochloric acid and the red tetrachlorgallein hydrate.[1] As the tetrachlorgallein hydrochloride is intensely colored, it must be a quinoid compound, as represented in the formulas given for this substance in the first article.[2]

Tetrachlorgallein Hydrate (Colored)

This substance, made from the pure monosodium salt by decomposing it with hydrochloric acid, has already been described.[3] It is insoluble in chloroform, benzene or ether, but dissolves readily in dry acetone, forming a practically *colorless* solution. Benzene and ether cause no precipitation when added to this solution but chloroform gives, on standing, a white precipitate of the *colorless* hydrate.[4] The addition of these solvents to the acetone solution produces no color. When diluted slightly with distilled water, however, the acetone solution becomes pink and turns cherry-red on further dilution, depositing a white precipitate of the carbinolcarboxylic acid. If the slightest trace of acid, even of acetic acid, be added to the water used to dilute the acetone solution, no color results. Methyl and ethyl alcohols, also dissolve the hydrate with a faint pink color, and dilution with distilled water gives a red color unless the water is previously acidified. Further dilution with water precipitates the carbinolcarboxylic acid.

It was thought desirable to determine whether the *blue* tetrasodium salt of tetrachlorgallein would give the same red hydrate[5] as the monosodium salt. Twelve grams of the pure monosodium salt were therefore slowly added to an actively boiling solution of 2.5 grams of sodium hydroxide in 2.5 liters of water, in a Jena glass flask. By keeping the solution boiling vigorously, the air was excluded and oxidation prevented. After solution was complete, an excess of dilute hydrochloric acid was added to the boiling solution. The precipitate formed had the same color and appearance as the red hydrate

[1] See page 22.
[2] THIS JOURNAL, **42**, 258.
[3] *Ibid.*, **43**, 220. See also p. 255 for its structural formula.
[4] See page 26.
[5] THIS JOURNAL, **43**, 220.

from the monosodium salt. It was filtered off, washed free from chlorides with hot water, dried in the air and analyzed.

Substance Gram	Loss at 157° Gram	Water Per cent.
0.3345	0.0121	3.62
0.2966	0.0108	3.64
0.3568	0.0127	3.56
	Calculated for $C_{20}H_8O_7Cl_4.H_2O$	3.47

Substance (dry) Gram	Tenth-normal silver nitrate cc.	Chlorine Per cent.
0.2830	22.51	28.21
0.2899	23.00	28.13
	Calculated for $C_{20}H_8O_7Cl_4$	28.26

Hence this product is also the colored hydrate. Its properties, too, show that it is identical with the red hydrate made from the monosodium salt.

As has already been stated,[1] the hydrochloric acid salt of tetrachlorgallein also yields the red hydrate. This hydrochloride was decomposed by boiling with water for thirty minutes, and the reddish precipitate was filtered off, washed free from hydrochloric acid, dried in the air and analyzed.

Substance Gram	Loss at 157° Gram	Water Per cent.
0.5375	0.0207	3.85
0.3061	0.0122	3.99
	Calculated for $C_{20}H_8O_7Cl_4.H_2O$	3.47

Substance (dry) Gram	Tenth-normal silver nitrate cc.	Chlorine Per cent.
0.2934	23.23	28.08
0.2554	20.33	28.23
	Calculated for $C_{20}H_8O_7Cl_4$	28.26

The properties of this product, as well as the analyses, show clearly that it is the colored tetrachlorgallein hydrate.

In determining the number of acetyl groups in tetrachlorgallein tetracetate[2] by the modified Wenzel method, a product was obtained which seemed to be the red hydrate. This mate-

[1] Page 21.

[2] THIS JOURNAL, **42**, 227.

rial was therefore investigated. Ten grams of the pure acetate were treated with 200 cc. of sulphuric acid (2 parts of pure concentrated sulphuric acid to one of distilled water) and the mixture heated in a boiling water bath for thirty minutes. The solution was then poured into cold water and the resulting precipitate washed by decantation six times with 800 cc. of distilled water. It was then filtered off, dried and placed in the apparatus used in determining acetyl groups. Thirty cc. of sulphuric acid were added and the mixture heated for a half-hour. Then 30 cc. of distilled water and 250 cc. of phosphoric acid mixture were added and the solution distilled in steam for one hour. No acetic acid was found in the distillate. Hence the saponification of the acetate was complete in the first operation. The mixture was poured into distilled water and the precipitate allowed to settle. The supernatant liquid was filtered and tested for hydrochloric acid but was found to contain none, so that no decomposition of the tetrachlorgallein had taken place. The precipitate was thoroughly washed with hot water and dried in the air. It was red and resembled the colored tetrachlorgallein hydrate in its chemical and physical properties, although it was distinctly darker in color than the red hydrate precipitated from the alkaline solution with hydrochloric acid.[1] Analyses, however, showed that this compound is really the colored hydrate containing a small quantity of the carbinolcarboxylic acid:

Substance Gram	Loss at 157° Gram	Water Per cent.
0.2728	0.0092	3.37
0.3019	0.0103	3.41
	Calculated for $C_{20}H_8O_7Cl_4.H_2O$	3.47

Substance (dry) Gram	Tenth-normal silver nitrate cc.	Chlorine Per cent.
0.2915	23.07	28.06
0.2729	21.56	28.01
	Calculated for $C_{20}H_8O_7Cl_4$	28.26

Some of the pure tetrachlorgallein diacetonate was dried at 170° and crystallized from 94 per cent. alcohol which was

[1] Page 21.

free from both acid and alkali. The crystals appeared almost colorless when observed with the magnifying glass in the highly colored solution. They were filtered off, washed with alcohol and with ether and dried in the air. The product was then reddish brown in color and gave all the reactions for tetrachlorgallein. It contained no ethyl ester, as it gave no color when treated with ether.[1] When heated to 157° in carbon dioxide for 12 hours, it gave off water but no alcohol or ether.

Substance Gram	Loss at 157° Gram	Water Per cent.
0.4429	0.0151	3.41
0.2947	0.0099	3.36
	Calculated for $C_{20}H_8O_7Cl_4.H_2O$	3.47

Substance (dry) Gram	Tenth-normal silver nitrate cc.	Chlorine Per cent.
0.2848	22.56	28.09
0.2761	21.91	28.13
	Calculated for $C_{20}H_8O_7Cl_4$	28.26

This substance is therefore the colored hydrate.

In order to obtain crystals for examination, some of the pure colored tetrachlorgallein hydrate was dissolved in 94 per cent. alcohol, and the solution filtered, heated to boiling and diluted with water very slowly. Fairly good crystals were thus obtained. They were submitted to Professor Gill, of the Mineralogical Department, who reports as follows:

Tetrachlorgallein Hydrate (*Colored*).—"The crystals occur as minute rhomboidal plates, the acute plane angle of the rhomboid measuring about 67°. Extinction takes place nearly parallel and normal to the shorter side of the rhomboid, less optical elasticity being the normal to this side. In convergent polarized light one axis appears eccentric near the edge of the field. From this optical behavior the crystals must be *triclinic*. They show a slight brownish red color and weak pleochroism. Possibly, if seen on edge, the color and pleochroism would be stronger. In mass the crystals are distinctly and strongly colored."

When a hot solution of the tetrachlorgallein diacetonate

[1] The ethyl ester, like the methyl ester, dissolves in ether with a red color.

in acetone is poured into *boiling* water, a reddish violet product results. This was investigated and found to be a mixture of the red hydrate and the carbinolcarboxylic acid. Analyses of the air-dried material gave the following results:

	Substance Gram	Loss at 157° Gram	Water Per cent.
I	0.3668	0.0137	3.73
II	0.4364	0.0162	3.71
	Calculated for $C_{20}H_8O_7Cl_4.H_2O$		3.47

No. II was afterwards heated for two hours at 175° and then two hours more at 202° but lost no further weight.

	Substance (dry) Gram	Tenth-normal silver nitrate cc.	Chlorine Per cent.
I	0.3000	23.51	27.79
II	0.2760	21.66	27.83
III	0.2524	19.73	27.72
Calculated for a mixture of equal parts of anhydrous tetrachlorgallein and the carbinolcarboxylic acid			27.77

Analysis III was made by the Pringsheim method.

A product very similar to this one was also obtained by the following method: 1.5 grams of sodium hydroxide purified by alcohol were dissolved in 900 cc. of distilled water, and the solution filtered and cooled to 0°. Five grams of pure tetrachlorgallein diacetonate were then added with vigorous stirring. The solution was filtered as rapidly as possible and acidified at 3° with dilute acetic acid. A dirty reddish precipitate was thrown down. This was filtered off, washed thoroughly and dried at room temperature. It was then analyzed:

Substance Gram	Loss at 157° Gram	Water Per cent.
0.3809	0.0168	4.41
	Calculated for $C_{20}H_8O_7Cl_4.H_2O$	3.47

Substance (dry) Gram	Tenth-normal silver nitrate cc.	Chlorine Per cent.
0.2845	22.28	27.77
Calculated for a mixture of equal parts of anhydrous tetrachlorgallein and the carbinolcarboxylic acid		27.77

This product, like the one made by saponifying the tetracetate with cold concentrated sulphuric acid and pouring the mixture into cold water,[1] is somewhat soluble in ether while the red hydrate is practically insoluble in this solvent. When the above alkaline solution was precipitated by a *mineral* acid instead of acetic acid[2] the red *hydrate* insoluble in ether was obtained under all conditions.

The carbinolcarboxylic acid also gave a product similar to the last two described. Fifteen grams of the pure compound were dissolved in 500 cc. of acetone, the solution filtered, heated to boiling and the acetone distilled off by passing in steam. A light reddish crystalline precipitate separated. This was filtered off and washed with water. It dried very quickly in the air. The following analyses show that it is a mixture of the red hydrate and the carbinolcarboxylic acid:

Substance Gram	Loss at 157° Gram	Water Per cent.
0.4218	0.0151	3.58
	Calculated for $C_{20}H_8O_7Cl_4.H_2O$	3.47

Substance (dry) Gram	Tenth-normal silver nitrate cc.	Chlorine Per cent.
0.2777	21.88	27.94
Calculated for a mixture of three parts of anhydrous tetrachlorgallein and one of the carbinolcarboxylic acid		28.01

Tetrachlorgallein Hydrate (Colorless)

This product was obtained in an attempt to prepare the carbinolcarboxylic acid in a crystallized condition. Sixteen grams of the pure, air-dried red tetrachlorgallein hydrate were dissolved in 250 cc. of freshly distilled acetone, the reddish brown solution filtered, cooled to 25° and about 20 cc. of distilled water added. No precipitate was formed. A slow stream of moist carbon dioxide, free from mineral acid, was then passed through the solution to remove some of the acetone and prevent oxidation. After several days *silvery white* needles crystallized out. This product was at first thought

[1] See THIS JOURNAL, **42**, 229.

[2] See page 37.

to be the carbinol acid. Analyses,[1] however, showed that it was a colorless hydrate of tetrachlorgallein.

Substance Gram	Loss at 157° Gram	Water Per cent.
0.5398	0.0192	3.56
0.5491	0.0204	3.72
	Calculated for $C_{20}H_8O_7Cl_4.H_2O$	3.47

Substance (dry) Gram	Tenth-normal silver nitrate cc.	Chlorine Per cent.
0.2675	21.34	28.29
	Calculated for $C_{20}H_8O_7Cl_4$	28.26

Another sample of the same product was dried to constant weight at 157° in a stream of dry hydrochloric acid gas and then heated in carbon dioxide at the same temperature until it ceased to lose weight.[2]

Substance Gram	Loss at 157° Gram	Water Per cent.
0.1609	0.0056	3.48
	Calculated for $C_{20}H_8O_7Cl_4.H_2O$	3.47

The chlorine in this product dried at 157° was then determined:

Substance Gram	Tenth-normal silver nitrate cc.	Chlorine Per cent.
0.1543	12.36	28.40
	Calculated for $C_{20}H_8O_7Cl_4$,	28.26

The crystals of the colorless hydrate were examined by Professor Gill who reports as follows: "Long colorless needles, the larger ones somewhat flattened. The end face makes an angle of about 80° with the long direction. Extinction angle about 35° to 38°, less optical elasticity lying in the direction of the arrow . The crystals were not large enough to give good optical figures in converged polarized light, but it could be seen that the substance is biaxial. It is probably *triclinic*, as all needles show inclined extinction."

This colorless hydrate is present in the crude tetrachlorgallein together with the red hydrate, and as it is less soluble

[1] These analyses were made by Mr. E. H. Nichols.
[2] These analyses were made by Mr. E. F. Hitch.

in methyl alcohol than the red hydrate it crystallizes out first, thus explaining the very light red color of this product.[1] The later fractions from methyl alcohol grow steadily deeper red in color and finally a dark red crystalline meal is obtained, identical with the product crystallized from ethyl alcohol.[2] It is quite probable that the material from which the diacetonate[3] was first obtained and which had a light yellowish gray color consisted very largely of this colorless hydrate. When the crude tetrachlorgallein is extracted with methyl alcohol, for the purpose of removing the zinc chloride and impurities, it is found that the undissolved material grows steadily *lighter* in color as the extraction proceeds, owing to the fact that the *red* hydrate is more soluble in methyl alcohol than the *colorless* hydrate.

The *colorless* hydrate exhibits almost the same chemical properties as the *red* compound. It loses one molecule of water at 157°, forming the anhydrous tetrachlorgallein, as shown by the analyses given above. This product, like the one tiaobned by heating the *red* hydrate and also the diacetonate to 157°, has only a *faint* color and is probably a lactoid form of tetrachlorgallein.[4] The *colorless* hydrate dissolves in dilute sodium carbonate solution with a red color and in excess of sodium hydroxide with the characteristic blue color given by all the forms of tetrachlorgallein (the hydrates, the anhydrous compound and the carbinol acid). When these solutions are treated with mineral acids, the *red* hydrate is precipitated. When exposed to dry hydrochloric acid gas, the *colorless* hydrate turns *red* at once and slowly absorbs hydrochloric acid, *at the same time losing water*, to form the same hydrochloride that the anhydrous tetrachlorgallein does.[5] The absorption of the hydrochloric acid takes place much more slowly than in the case of the *red* hydrate, 240 hours being required before constant weight is attained. This difference in conduct of the two hydrates is due to the difference in structure. The

[1] See page 8 for the analyses.
[2] See page 24.
[3] See page 1.
[4] See page 12.
[5] Compare this conduct with that of the *red* hydrate, see page 30.

red hydrate is already a *quinoid* compound and can absorb hydrochloric acid directly to form the *hydrochloride of the hydrate*, while the *colorless* hydrate must first lose water and be transformed into the quinoid condition before it can unite with hydrochloric acid, forming the *hydrochloride of the anhydrous tetrachlorgallein*. Experimental data:[1]

Tetrachlorgallein hydrate (colorless) Gram	Anhydrous tetrachlorgallein Gram	Tenth-normal sodium hydroxide cc.	Hydrochloric acid absorbed Per cent.	Water lost Per cent.
0.1765	0.1699	3.04	6.28	3.74
Calculated for the formation of $C_{20}H_8O_7Cl_4.HCl$ from $C_{20}H_8O_7Cl_4.H_2O$ with loss of H_2O			7.01	3.47

With dry ammonia gas the *colorless* hydrate acts exactly like the *colored* hydrate,[2] losing water and forming at once the colored tetrammonium salt, as shown by the following experiment made by Mr. E. F. Hitch:

Tetrachlorgallein hydrate (colorless) Gram	Gain in weight Gram	Tenth-normal hydrochloric acid cc.	Ammonia absorbed Per cent.	Gain in weight Per cent.	Water lost Per cent.
0.2074	0.0199	15.93	13.08	9.60	3.48
Calculated for the formation of $C_{20}H_4O_7Cl_4.(NH_4)_4$ from $C_{20}H_8O_7Cl_4.H_2O$ with loss of H_2O			13.11	9.64	3.47

As the *colorless* hydrate must have the *lactoid* structure, it follows that the transformation of the *lactoid* to the *quinoid* condition can take place in *solids* as well as in solution.

When the *colorless* hydrate is dissolved in acetone or methyl alcohol and the solution is poured into a large quantity of acidified water, the carbinol acid is precipitated.[3] If the acetone solution of the *colorless* hydrate be concentrated by

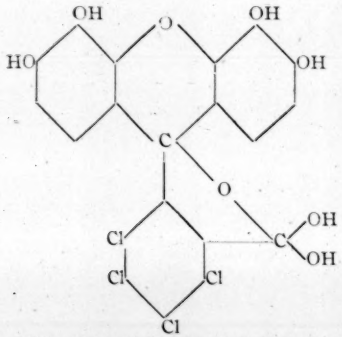
[1] This experiment was made by Mr. E. F. Hitch. See page 30 for details of the method.

[2] See page 33 for details of the method.

[3] See page 37.

distilling off a sufficient amount of the acetone, the diacetonate[1] crystallizes out.

As this hydrate is a *colorless* compound, it must have the *lactoid* structure and the following formula is suggested for it:



Tetrachlorgallein Hydrate (colorless)

The influence of the chlorine in the phthalic acid part of the compound on the stability of a molecule containing a carbon atom united to *two* or *three* hydroxyl groups shows itself very clearly in these hydrates and in the carbinolcarboxylic acid.[2]

Action of Dry Hydrochloric Acid Gas on the Red Tetrachlorgallein Hydrate

The air-dried red hydrate made from the blue tetrasodium salt of tetrachlorgallein[3] was placed in a stream of hydrochloric acid gas dried with phosphorus pentoxide. It became much darker red in color and absorbed slightly more than one molecule of hydrochloric acid:

Tetrachlorgallein hydrate Gram	Gain in weight Gram	Hydrochloric acid Per cent.
0.4296	0.0330	7.13
Calculated for $C_{20}H_8O_7Cl_4.H_2O.HCl$		6.38

[1] See page 8.

[2] See also the article on tetrachlorphthalic acid.—THIS JOURNAL, **41**, 411.

[3] See page 21.

This hydrochloride was then heated at 157° in carbon dioxide and lost both water and hydrochloric acid:

Substance Gram	Total loss at 157° Gram	Hydrochloric acid Gram	Water Gram	Water Per cent.[1]
0.4626	0.0481	0.0330	0.0151	3.51
		Calculated for $C_{20}H_8O_7Cl_4.H_2O$		3.47

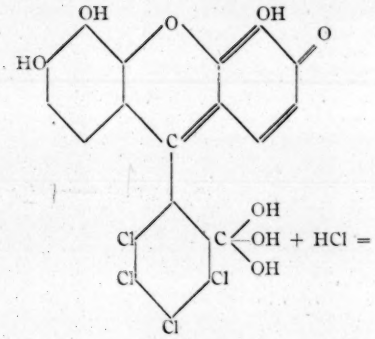
Hence the colored hydrate takes up one molecule of hydrochloric acid to form a hydrochloride but *without loss of water*. In this respect it differs very markedly from the colorless hydrate which forms the hydrochloride only by the loss of a molecule of water.[2]

The anhydrous tetrachlorgallein obtained by heating some of this hydrochloride to 157° also absorbs approximately one molecule of hydrochloric acid.[3]

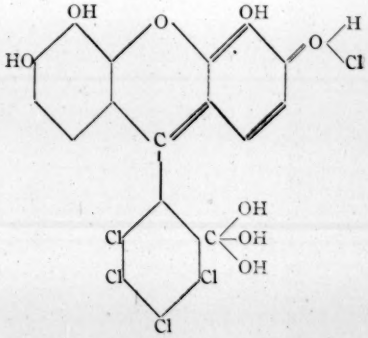
Anhydrous tetrachlorgallein Gram.	Gain in weight Gram	Hydrochloric acid Per cent.
0.3439	0.0267	7.20
	Calculated for $C_{20}H_8O_7Cl_4.HCl$	6.77

The formation of the hydrochloride of the *red* hydrate may be regarded as a confirmation of the formula given for the *colored* tetrachlorgallein hydrate. If this formula be compared with that assigned to tetrachlorgallein hydrochloride,[4] it will be seen that it admits of the formation of a hydrochloride of the colored hydrate without the loss of water:

[1] Per cent. of the original *hydrate* used.
[2] See page 29.
[3] Compare page 19.
[4] THIS JOURNAL, **42**, 255 and 258.



Red Hydrate



Hydrochloride of Red Tetrachlorgallein Hydrate

Action of Dry Ammonia on the Red Tetrachlorgallein Hydrate

Tetrammonium Salt of Tetrachlorgallein.—The colored hydrate combines very readily with dry ammonia gas, forming a tetrammonium salt and at the same time losing a molecule of water. This was shown by determining first the increase in weight (which represents the weight of ammonia absorbed

by the hydrate minus the weight of the water lost), secondly, by determining the amount of ammonia actually present in the ammonium salt. The colored hydrate used was that obtained from the blue sodium salt and was some of the same product made use of in the preparation of the hydrochloride.[1] A weighed portion of this red hydrate in a boat was kept in a stream of dry ammonia gas, at room temperature, until it came to constant weight, the boat and its contents being quickly transferred, before weighing, to a tube with a tightly fitting stopper. This tube was then opened under water containing a measured volume of tenth-normal hydrochloric acid, the mixture stirred to ensure complete decomposition of the ammonium salt and the excess of hydrochloric acid titrated with tenth-normal ammonia solution, the red tetrachlorgallein hydrate set free acting as the indicator. The amount of water lost by the red hydrate used is then found by subtracting the gain in weight from the amount of ammonia actually present in the ammonium salt:

	Substance Gram	Gain in weight Gram	Tenth-normal hydrochloric acid cc.	Ammonia absorbed Per cent.	Gain in weight Per cent.	Water lost Per cent.
I	0.2278	0.0215	17.19	12.85	9.44	3.41
II	0.2472	0.0231	18.35	12.64	9.34	3.30
Calculated for the formation of $C_{20}H_4O_7Cl_4(NH_4)_4$ from $C_{20}H_8O_7Cl_4.H_2O$ with loss of H_2O				13.11	9.64	3.47

In Analysis II a trace of ammonia was lost owing to the stopper of the weighing tube becoming loose before it was completely immersed in the hydrochloric acid solution. The formation of the ammonium salt is complete in about half an hour. It is a bluish black compound which dissolves in water with a deep purple color and is extremely easily oxidized either in the solid form or in solution. It loses most of its ammonia so readily that it can be weighed only in a closed tube. When acids are added to its solution in water, the red tetrachlorgallein hydrate is precipitated. The same tetrammonium salt was also obtained by exposing the carbinol-

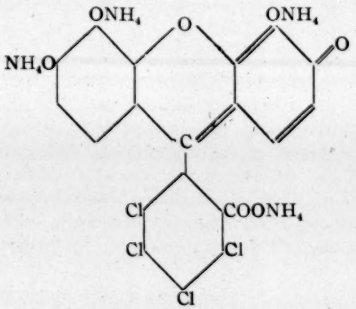
[1] See pages 21 and 30.

carboxylic acid and the colorless hydrate to the action of dry ammonia gas.[1] Furthermore, anhydrous tetrachlorgallein, made by heating the pure diacetonate to constant weight at 157°, also absorbs ammonia with the evolution of considerable heat and a marked increase in volume, forming the same bluish black tetrammonium salt. The same precautions in weighing were observed to prevent loss of ammonia.

Tetrachlorgallein Gram	Gain in weight Gram	Ammonia absorbed Per cent.
0.3293	0.0440	13.36
0.4159	0.0559	13.44
Calculated for formation of $C_{20}H_4O_7Cl_4(NH_4)_4$		13.58

This salt was placed in a Hempel desiccator with concentrated sulphuric acid above it and allowed to stand in the hope that it would come to constant weight. The loss was very rapid at first, amounting, after two hours, to two-thirds of the original ammonia. The rate of loss gradually became less but constant weight was never attained, though there was evidence of the formation of a *mono* ammonium salt which loses some of its ammonia very slowly.

The structure of the tetrammonium salt is best represented as follows:



Tetrammonium Salt of Tetrachlorgallein (colored)

[1] **See pages 29 and 48.**

Monoammonium Salt of Tetrachlorgallein

Preparation.—Five and two-tenths grams of the colored tetrachlorgallein hydrate were dissolved in 300 cc. of absolute alcohol by the aid of gentle heat, the solution filtered and cooled to about 35°, and 11.3 cc. of 0.731 normal aqueous ammonia were added drop by drop from a burette, the solution being shaken constantly. The weight of anhydrous ammonia corresponding to the above amount of aqueous ammonia is 0.14 gram while the amount required to combine with the 5.2 grams of the hydrate to form the monoammonium salt is 0.17 gram. Hence the tetrachlorgallein hydrate was in excess. The alcoholic solution turned a deep red on the addition of the ammonia but no precipitate formed until all the ammonia had been added and the solution had been agitated for several minutes. Then very fine dark needles began to appear and the crystallization was complete after about 90 minutes. The crystals were filtered off, washed with 94 per cent. alcohol, spread out on filter paper and let stand in the air for 40 hours. They were then analyzed as follows: A weighed amount in a platinum boat was placed in the drying apparatus[1] and hydrogen, purified by concentrated sulphuric acid, 10 per cent. caustic potash solution, calcium chloride and phosphorus pentoxide in succession, was passed over it. The other end of the drying apparatus was connected with a Hugershoff gas wash bottle containing a measured amount of standard hydrochloric acid properly diluted. The boat was then heated to 160° until the substance lost no further weight, which required about three hours. The total loss in weight was due entirely to loss of ammonia and of *water*, as the solution in the Hugershoff wash bottle was tested for alcohol by means of the iodoform reaction but none was present. Considerable water was given off and condensed on the cold part of the tube. The ammonia in the wash bottle was determined by titrating the excess of standard hydrochloric acid with tenth-normal sodium hydroxide solution and cochineal. The difference between the total loss and the weight of ammonia found by titration is evidently

[1] THIS JOURNAL, **41**, 403.

due to water. The dry residue was then placed in a measured amount of tenth-normal hydrochloric acid and the mixture heated to ensure the complete decomposition of the ammonium salt. It was then cooled, transferred to a porcelain dish and the excess of hydrochloric acid titrated with tenth-normal sodium hydroxide solution, the colored tetrachlorgallein hydrate set free acting as the indicator.

	Substance Gram	Loss at 160° Gram	Tenth-normal hydrochloric acid: For volatilized ammonia cc.	Tenth-normal hydrochloric acid: For ammonia in residue cc.
I	0.2701	0.0334	2.50	2.05
II	0.2894	0.0360	2.73	2.07

	Loss at 160° Per cent.	Ammonia volatilized Per cent.	Ammonia in residue Per cent.	Total ammonia Per cent.	Water lost Per cent.
I	12.37	1.58	1.29	2.87	10.79
II	12.44	1.61	1.22	2.83	10.83
Calculated for $C_{20}H_7O_7Cl_4(NH_4)\cdot 3.5H_2O$				2.93	10.84

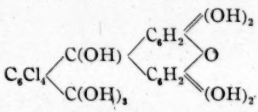
These analyses show that this compound is the mono-ammonium salt of tetrachlorgallein having the formula $C_{20}H_7O_7Cl_4(NH_4)\cdot 3.5H_2O$. All the water and over half the ammonia are driven off at 160°. Since the pure colored tetrachlorgallein hydrate, which had been previously analyzed, was used in making the salt, chlorine determinations would be superfluous.

Properties.—The compound is beautifully crystallized, consisting, as seen under the microscope, of slender prisms, which are red in transmitted light and almost black in reflected light. In bulk, the salt is nearly black with a faint bronzy luster. It dissolves in water, giving a *red* solution, but part of the salt is hydrolyzed and some of the red tetrachlorgallein hydrate is precipitated as in the case of the sodium and potassium salts.[1] The compound does not lose ammonia in the air at room temperature, as shown by the fact that the product analyzed had stood for 40 hours. It dissolves slightly in cold absolute alcohol with a pink color. When heated with absolute alcohol, it dissolves rather easily but with decomposition,

[1] THIS JOURNAL, **42**, 215 and 218.

ammonia being evolved. It is insoluble in cold acetone and is partially decomposed by boiling acetone, with the loss of ammonia. In ether, benzene and other neutral organic solvents, it is insoluble. Its structure is similar to that of the monosodium and monopotassium salts of tetrachlorgallein and is given by the formula on page 259 in the first article.[1]

Tetrachlorgalleincarbinolcarboxylic Acid



This compound was first obtained by dissolving the pure diacetonate in hot acetone, cooling and diluting the *cold* solution with *cold* water. The colorless acetone solution became red and then, on the addition of more water, an almost colorless precipitate was thrown down. The mixture was divided into two parts. One was filtered, the precipitate washed with cold water and dried at room temperature. The other portion was boiled for one hour after the addition of a little acetic acid, filtered hot and the precipitate, after thorough washing with hot water, dried at 25°. The two products looked exactly alike and were very nearly white. The product which had been boiled was analyzed.

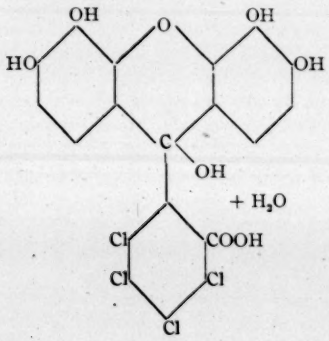
Substance Gram	Loss at 157° Gram	Water Per cent.
0.3278	0.0129	3.94
0.3796	0.0148	3.90
	Calculated for $C_{20}H_{10}O_8Cl_4.H_2O$	3.35

A chlorine determination on the substance dried at 157° gave the following result:

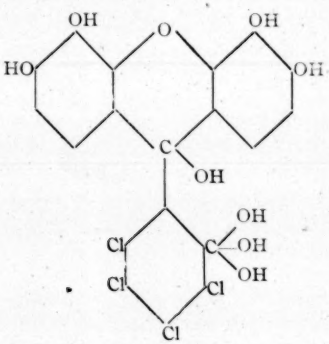
Substance Gram	Tenth-normal silver nitrate cc.	Chlorine Per cent.
0.3145	24.26	27.35
	Calculated for $C_{20}H_{10}O_8Cl_4$	27.28

[1] See THIS JOURNAL, **42**.

The compound, dried at 157°, therefore contains one molecule of water more than the anhydrous tetrachlorgallein, $C_{20}H_8O_7Cl_4$. In order to drive off this water, the substance dried at 157° was heated in carbon dioxide to 203° but lost very little weight even at this high temperature, less than 0.4 per cent. The extra molecule of water which the dried substance contains must therefore be represented as water of constitution. This compound dissolves in excess of caustic alkalies with a blue color and gives all the characteristic reactions of the red tetrachlorgallein hydrate, but while this hydrate is *colored* and loses a molecule of water when heated to 157°, giving the anhydrous tetrachlorgallein, the carbinol acid is *white* and also loses a molecule of water at 157°, but the resulting product, though *colorless*, still differs from the anhydrous tetrachlorgallein by one molecule of water which can not be driven off even at 203°. The compound is therefore the carbinolcarboxylic acid:



or



Tetrachlorgalleincarbinolcarboxylic Acid

The molecule of water which is given off at 157° is represented in the second formula as present in the same form as in the colored tetrachlorgallein hydrate and for the same reasons.[1]

A second preparation was made from another lot of the diacetonate, which was first recrystallized from acetone and then dissolved in pure dry acetone. This solution was filtered, cooled and poured slowly and with constant stirring into 2.5 liters of distilled water containing a trace of hydrochloric acid and previously cooled to 13°. A faintly pink precipitate was at once thrown down. The mixture was then heated to boiling for thirty minutes by passing in steam, the solution at once filtered, and the precipitate washed with distilled water and dried in the air at room temperature. The product dried to constant weight at 157° was then analyzed for chlorine.

Substance Gram	Tenth-normal silver nitrate cc.	Chlorine Per cent.
0.2875	22.14	27.31
0.2402	18.43	27.21
	Calculated for $C_{20}H_{10}O_8Cl_4$	27.28

[1] See THIS JOURNAL, **42**, 255.

Some of the diacetonate made by Mr. Briggs[1] was dissolved in acetone and the pale red solution added to a large excess of cold water acidified with hydrochloric acid. The precipitate was filtered off, washed thoroughly with water and dried to constant weight in a water oven. It was almost colorless, having a faint pink tinge due to the presence of a minute quantity of the colored hydrate. Analysis:[2]

Substance (dry) Gram	Tenth-normal silver nitrate cc.	Chlorine Per cent.
0.3091	23.81	27.32
	Calculated for $C_{20}H_{10}O_8Cl_4$	27.28

In purifying the crude tetrachlorgallein by recrystallization from methyl alcohol, it was noted that the methyl alcohol solution, when poured into a large quantity of cold water, gave a very light colored product resembling that obtained in a similar manner from the acetone solution. Analyses by Mr. Briggs show that this product is also the carbinol acid:

Substance (dried at 158°) Gram	Tenth-normal silver nitrate cc.	Chlorine Per cent.
0.2543	19.59	27.31
0.2511	19.38	27.37
	Calculated for $C_{20}H_{10}O_8Cl_4$	27.28

When the ethyl alcohol or glacial acetic acid solution of tetrachlorgallein is diluted with water, the precipitate formed is also very light colored and is probably the carbinol acid.

The carbinol acid was also made by Mr. Briggs from the tetrachlorgallein tetracetate. About four grams of the pure tetracetate were dissolved by heating on a water bath in 50 cc. of pure concentrated sulphuric acid in an atmosphere of carbon dioxide. The deep red solution thus obtained was cooled and poured slowly, with constant stirring, into 100 cc. of methyl alcohol kept cold in a freezing mixture. This solution was then poured into a large volume of cold water, the precipitate washed thoroughly and dried in the air. Analyses gave the following results:

[1] See page 8.

[2] Made by Mr. Briggs.

Substance Gram	Loss at 158° Gram	Water Per cent.
0.2406	0.0138	5.74
0.2471	0.0142	5.75
	Calculated for $C_{20}H_{10}O_8Cl_4.H_2O$	3.35
	Calculated for $C_{20}H_{10}O_8Cl_4.2H_2O$	6.49

Substance (dried at 158°) Gram	Tenth-normal silver nitrate cc.	Chlorine Per cent.
0.2268	17.45	27.28
0.2329	17.93	27.30
	Calculated for $C_{20}H_{10}O_8Cl_4$	27.28

When the tetracetate is hydrolyzed with concentrated sulphuric acid and the resulting solution poured directly *into ice water*, a *reddish* precipitate is formed consisting of the *red* hydrate and a small amount of the colorless carbinol acid, as the following analyses by Mr. Briggs show:[1]

Substance Gram	Loss at 158° Gram	Water Per cent.
0.2592	0.0095	3.66
0.2626	0.0094	3.59
	Calculated for $C_{20}H_8O_7Cl_4.H_2O$	3.47

Substance (dried at 158°) Gram	Tenth-normal silver nitrate cc.	Chlorine Per cent.
0.2497	19.75	28.05
0.2351	18.54	27.97
	Calculated for $C_{20}H_8O_7Cl_4$	28.26

The carbinol acid is also obtained when an acetone solution of the red hydrate is poured into a large quantity of ice water acidified with hydrochloric acid. Analysis by Mr. Briggs:

Substance (dry) Gram	Tenth-normal silver nitrate cc.	Chlorine Per cent.
0.2164	16.63	27.25
	Calculated for $C_{20}H_{10}O_8Cl_4$	27.28

The anhydrous tetrachorgallein made by heating the diacetonate to 158° also gives the carbinol acid when its acetone solution is poured into a large volume of ice water.[2]

The light colored hydrate obtained by crystallizing the

[1] See *also* page 23.

[2] See page 48.

crude tetrachlorgallein several times from methyl alcohol, and which is essentially the *colorless* hydrate containing a trace of the *colored* hydrate, also gives the carbinol acid when it is dissolved in acetone and the solution is poured into cold water acidified with hydrochloric acid, as shown by the following analysis made by Mr. Briggs:

Substance (dry) Gram	Tenth-normal silver nitrate cc.	Chlorine Per cent.
0.2112	16.28	27.33
	Calculated for $C_{20}H_{10}O_8Cl_4$	27.28

All the forms, therefore, of tetrachlorgallein (the *colorless* hydrate, the *colored* hydrate and the anhydrous product), as well as the *colorless* diacetonate, give the carbinol acid when precipitated from acetone solution by water.

Many attempts were made to obtain the carbinol acid in crystals but without success, as it was found that the colorless hydrate or a mixture of the two hydrates crystallized out in every case. A well crystallized product having almost no color and obtained by crystallizing the carbinol acid from dilute acetone was analyzed by Mr. Briggs:

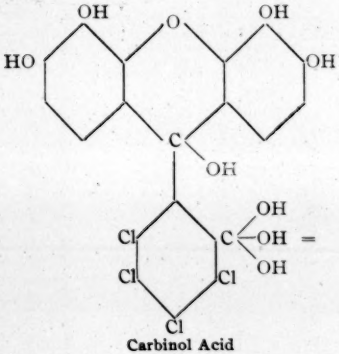
Substance Gram	Loss at 157° Gram	Water Per cent.
0.2625	0.0096	3.66
	Calculated for $C_{20}H_8O_7Cl_4.H_2O$	3.47

Substance (dry) Gram	Tenth-normal silver nitrate cc.	Chlorine Per cent.
0.2525	19.99	28.08
	Calculated for $C_{20}H_8O_7Cl_4$	28.26

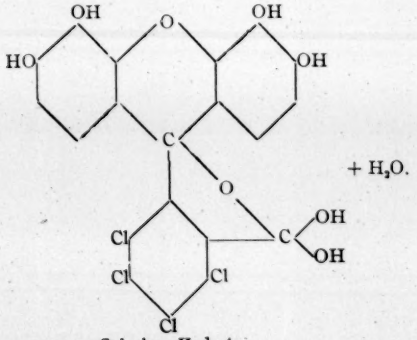
These results show that the compound is the colorless hydrate. The same product was obtained from methyl and ethyl alcohols in attempts to crystallize the *carbinol acid* from these solvents, though in this case it was more highly colored and hence contained more of the *colored* hydrate. The *colored* hydrate, itself, when crystallized from any of these solvents, is partially converted into the *colorless* hydrate, which crystallizes out first in the characteristic white needles. Owing to this easy conversion of the *colored* into the *colorless* hydrate, it is doubtful

whether the *red* hydrate has ever been prepared entirely free from its colorless isomer. To get the colorless hydrate pure is a comparatively easy matter, the presence of the slightest trace of the red isomer being shown at once by the color of the product.

The transformation of the carbinol acid into the colorless hydrate can be readily understood from the following equation:

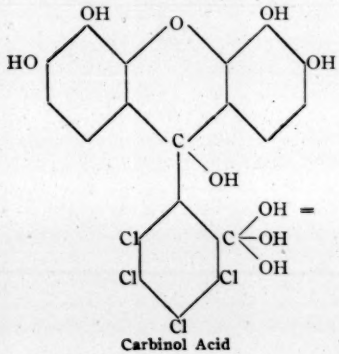


Carbinol Acid

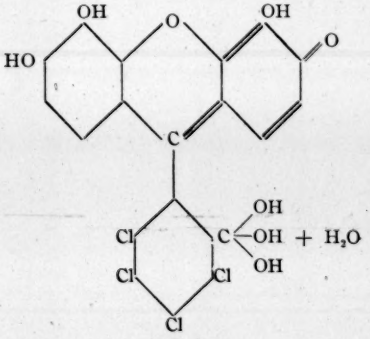


Colorless Hydrate

A certain amount of the carbinol acid is converted into the *colored* hydrate at the same time, the amount depending upon the boiling point of the solvent. For example, the crystals from acetone are almost colorless while those from methyl and especially from ethyl alcohol are more highly colored. This conversion is represented as follows:

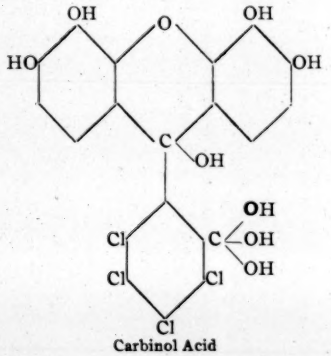


Carbinol Acid

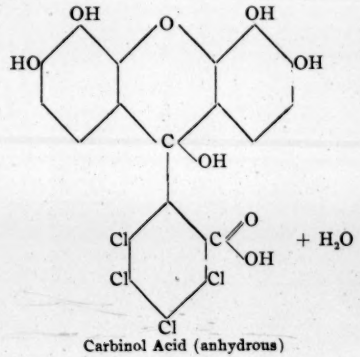


Colored Hydrate

When heated to 158°, the carbinol acid loses water from a different part of the molecule and gives the anhydrous carbinol acid:



Carbinol Acid



Carbinol Acid (anhydrous)

Attempts were made to crystallize the *anhydrous* carbinol acid from dry acetone and from absolute methyl alcohol but analyses showed that the products obtained were mixtures of the hydrates and the carbinol acid.

Action of Hydrochloric Acid on Tetrachlorgalleincarbinolcarboxylic Acid

It was found that the colorless carbinolcarboxylic acid, dried at 157°, takes up hydrochloric acid, when placed in an atmosphere of the dry gas at room temperature, to form a *colored* hydrochloride and it seemed probable that it would give the same product that the red tetrachlorgallein hydrate does[1] and hence would lose a molecule of water and of hydrochloric acid on heating to 157°. Some of the pure carbinolcarboxylic acid was therefore dried to constant weight at 158° and put in an atmosphere of dry hydrochloric acid gas at room temperature. It turned red at once and gradually gained weight until it had absorbed one molecule of hydrochloric acid, after which it began to lose weight. This loss proved to be due to water but was so slow that the red hydrochloride was heated to 157° in an atmosphere of carbon dioxide. Both water and hydrochloric acid were evolved. The latter was absorbed in distilled water in a Hugershoff gas wash bottle and the amount determined by titration with standard sodium hydroxide solution. The residue dried at 157° was then weighed and shown to be anhydrous tetrachlorgallein by analysis:

Tetrachlorgalleincarbinolcarboxylic acid Gram	Anhydrous tetrachlorgallein Gram	Tenth-normal sodium hydroxide cc.	Hydrochloric acid absorbed Per cent.	Water lost Per cent.
0.4024	0.3897	7.97	7.22	3.16
0.6417	0.6205	12.80	7.27	3.30
Calculated for formation of $C_{20}H_8O_7Cl_4.HCl$ from $C_{20}H_{10}O_8Cl_4$			7.01	3.47

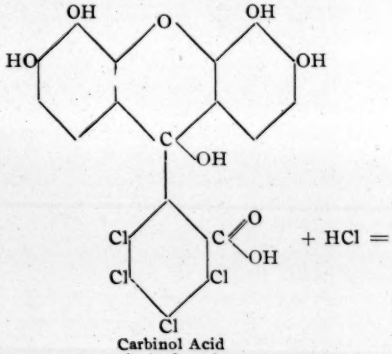
The chlorine in the material dried at 157° was then determined:

Substance Gram	Tenth-normal silver nitrate cc.	Chlorine Per cent.
0.2740	21.70	28.08
	Calculated for $C_{20}H_8O_7Cl_4$	28.26

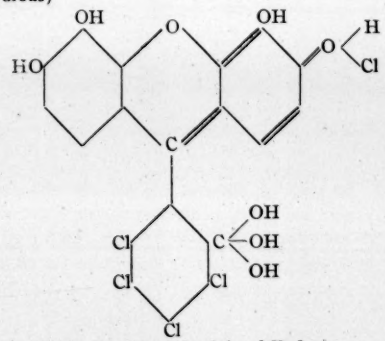
These results show that the dried, *colorless* carbinolcarboxylic acid, which loses no weight even when heated to 203°, takes up hydrochloric acid to form a colored hydrochloride

[1] See page 30.

and this, when heated to 157°, loses both hydrochloric acid and water, giving the anhydrous tetrachlorgallein. This furnishes a most striking proof of the structure of the carbinol-carboxylic acid.[1] It is quite likely that the hydrochloride of the colored hydrate is formed here, as the carbinol acid gains in weight until it has absorbed an amount equivalent to one molecule of hydrochloric acid, after which it slowly loses weight due to the loss of water. The reaction may be represented as follows:



Carbinol Acid (anhydrous)



Hydrochloride of the Colored Hydrate

[1] See page 39.

Action of Dry Ammonia on Tetrachlorgalleincarbinolcarboxylic Acid

The colorless carbinol acid, dried at 157°, takes up ammonia at ordinary temperatures, when placed in an atmosphere of the dry gas, forming the same bluish black tetrammonium salt that the hydrates do,[1] and loses a molecule of water. The carbinol acid used was made from the anhydrous tetrachlorgallein obtained by heating the diacetonate to constant weight at 157°. This product was dissolved in acetone, the solution cooled to 8° and diluted with a large volume of cold distilled water containing a little hydrochloric acid. The precipitated carbinol acid was suspended in hot alcohol, filtered, washed with alcohol, dried in the air and then heated to constant weight at 157°. A weighed quantity was then exposed to the action of dry ammonia at ordinary temperature until it came to constant weight, for which one hour was sufficient. The gain in weight was then obtained directly and the ammonia absorbed was determined by decomposing the tetrammonium salt with a measured amount of standard hydrochloric acid and titrating the excess of acid with standard ammonia solution, the red tetrachlorgallein hydrate set free[2] acting as the indicator. The water lost in the formation of the tetrammonium salt was then obtained by subtracting the gain in weight from the amount of ammonia absorbed.

Carbinol acid (dried at 157°) Gram	Gain in weight Gram	Tenth-normal hydrochloric acid cc.	Gain in weight Per cent.	Ammonia absorbed Per cent.	Water lost Per cent.
0.2262	0.0203	15.95	8.97	12.01	3.04
0.3120	0.0291	22.60	9.33	12.34	3.01
0.2208	0.0226	17.18	10.24	13.25	3.01
Calculated for conversion of $C_{20}H_{10}O_9Cl_4$ into $C_{20}H_4O_7Cl_4(NH_4)_4$			9.64	13.11	3.47

Hence the colorless tetrachlorgalleincarbinolcarboxylic acid, which had been dried to constant weight at 157,° loses water of constitution *at room temperature* in an atmosphere of dry ammonia and absorbs ammonia, forming the colored tetra-

[1] See pages 29 and 32.
[2] See page 33.

chlorgallein tetrammonium salt. A comparison of the structural formula for this salt[1] with the one given for the carbinolcarboxylic acid[2] shows that its formation from the carbinol acid, dried at 157°, is possible only by the loss of a molecule of water of constitution.

Potassium Salt made from the Tetrachlorgalleincarbinolcarboxylic Acid

A solution of 12 grams of the air-dried carbinol acid in 600 cc. of 94 per cent. alcohol was heated to boiling in a flask connected with a reflux condenser. Alcohol vapor was passed into this solution through a tube reaching to the bottom of the flask. By this means the mixture was kept constantly agitated and all the air was expelled from the flask, thus preventing oxidation. A filtered solution of 3 grams of pure potassium acetate in 100 cc. of 94 per cent. alcohol was then slowly added to the boiling liquid through the condenser. The potassium salt was filtered off after boiling for 30 minutes, boiled again with 600 cc. of fresh 94 per cent. alcohol, filtered, washed with alcohol, dried in the air several days and analyzed. It contained water of crystallization which was determined by heating the salt to 157° for three hours in a stream of pure hydrogen in the drying apparatus.[3] An examination of the vapors given off showed that they contained no alcohol. The loss at 157° was, therefore, due to water, considerable moisture condensing on the cold part of the drying tube.

Substance Gram	Loss at 157° Gram	Water Per cent.
0.3073	0.0327	10.64
0.3000	0.0320	10.67
Calculated for $C_{20}H_7O_7Cl_4K.3.5H_2O$		10.46

The chlorine in the material dried at 157° was determined by the modified lime method[4] and the potassium by decomposing a weighed quantity with a measured amount of standard hydrochloric acid and titrating the excess of the hydrochloric

[1] Page 34.
[2] See page 39.
[3] This Journal, 41, 403.
[4] *Ibid.*, 41, 397.

acid with standard alkali, the red tetrachlorgallein hydrate set free acting as the indicator.[1]

Substance Gram	Tenth-normal silver nitrate cc.	Chlorine Per cent.
0.2739	20.13	26.07
0.2519	18.53	26.09
	Calculated for $C_{20}H_7O_7Cl_4K$	26.26

Substance Gram	Tenth-normal hydrochloric acid cc.	Potassium Per cent.
0.4894	8.86	7.09
0.6625	12.00	7.09
	Calculated for $C_{20}H_7O_7Cl_4K$	7.25

This compound is, therefore, the monopotassium salt of tetrachlorgallein and its properties are also identical with those of the potassium salt made from the anhydrous tetrachlorgallein and from the red hydrate.[2] The crystals, which are dark brown, dissolve in water with a red color, at the same time undergoing partial hydrolysis with precipitation of a small amount of the colored tetrachlorgallein hydrate. Acids precipitate the red hydrate from the aqueous solution completely. With regard to the crystallography of the salt, Professor Gill reports as follows: "The substance occurs in minute columnar crystals 0.002 to 0.004 mm. in thickness, and 0.01 to 0.02 mm. long. They show strong pleochroism, changing from nearly colorless to deep purplish brown on rotation in transmitted polarized light. Interference colors between crossed Nicols are of lower first order, indicating fairly strong double refraction, probably 0.060 to 0.080. An extinction angle of 20° to 25° proves the substance to be either monoclinic or triclinic in crystallization but no optical figure could be obtained, on account of the very small size of the crystals."

The structural formula for this colored monopotassium salt of tetrachlorgallein has already been given.[3]

Baeyer,[4] after his very thorough investigation of the con-

[1] See THIS JOURNAL, **42**, 216.
[2] *Ibid.*, **42**, 217 to 219.
[3] *Ibid.*, **42**, 259.
[4] Ann. Chem. (Liebig), **354**, 152.

nection between color and chemical composition in the case of the derivatives of triphenylcarbinol, finds that *all carbinols are colorless; color appears only in consequence of the elimination of water from the molecule.* This conclusion is strikingly confirmed by the conversion of the *colorless* tetrachlorgallein-carbinolcarboxylic acid into the three *colored* compounds, the hydrochloride, the ammonium salt and the potassium salt.[1] By means of these compounds it is possible to convert the *colorless* carbinol acid into the *colored* hydrate, for the hydrochloride gives this hydrate when boiled with water and the two salts give the same product when their aqueous solutions are decomposed with acids. It is not necessary to isolate the compounds. Thus if the carbinol acid is dissolved in caustic alkali and acid is added to the solution, the red hydrate is precipitated. This may then be reconverted into the colorless carbinol acid by dissolving in acetone and precipitating with cold water. The anhydrous tetrachlorgallein may be obtained from the carbinolcarboxylic acid most readily by treating the latter at room temperature with dry hydrochloric acid gas until it ceases to gain weight and then heating the product to 158°.

Action of Acetic Anhydride on Tetrachlorgalleincarbinolcarboxylic Acid

It was thought possible that the presence of the five alcoholic hydroxyl groups in the carbinol acid might be shown by making a pentacetate. Five grams of the pure white carbinol acid were therefore boiled with 30 cc. of acetic anhydride for one hour. The solution had a dark brown color but showed no fluorescence. Fifty cc. of methyl alcohol were then added to the cold solution and the mixture heated to boiling to convert the excess of acetic anhydride into methyl acetate. The solution became almost solid from the separation of the tetrachlorgallein acetate. More methyl alcohol was therefore added and the mixture boiled. The tetracetate, which was almost pure white and beautifully crystallized, dissolved

[1] Although the air-dried potassium salt contains water of crystallization, still this is entirely driven off at 157° while the carbinol acid itself is stable at 203°.

only to a slight extent. The crystals were filtered off, washed with methyl alcohol and dried. They were found to be insoluble in sodium carbonate solution even on heating. This fact indicated that the product was not an acid and hence that it was not the pentacetate of the carbinolcarboxylic acid. The white crude acetate melted at 250°–252° (uncor.) but became pink much below this temperature, thus indicating that the compound was the tetrachlorgallein tetracetate. It was, therefore, purified by crystallization from benzene.[1] The crystals were then pure white and melted sharply at 260° (cor.), the melting point of the tetracetate, and also showed the same marked contraction at 150°–160° noted in the case of the tetracetate made from the anhydrous tetrachlorgallein.

A chlorine determination on the substance dried to constant weight at 100° in an atmosphere of carbon dioxide gave further proof that this product really was tetrachlorgallein tetracetate:

Substance Gram	Tenth-normal silver nitrate cc.	Chlorine Per cent.
0.3692	21.97	21.10
	Calculated for $C_{20}H_4O_7Cl_4(C_2H_3O)_4$	21.17

The carbinol acid then gives tetrachlorgallein tetracetate, a *colorless* product having the *lactoid* structure,[2] when heated, with acetic anhydride, thus showing that the elimination of water from the carbinol acid does not necessarily give a *colored* compound. The product formed from the carbinol acid by the loss of water must have the *quinoid* structure in order that a colored compound may result.

Preparation of Tetrachlorgallein Hydrate

As it seemed probable that the long and tedious heating of the tetrachlorphthalic acid to 100° to convert it into the anhydride might be avoided, Mr. Briggs, at our suggestion, endeavored to make tetrachlorgallein hydrate directly from the tetrachlorphthalic acid, using 155 grams of the acid, 135 grams of pyrogallol and 70 grams of freshly fused zinc chloride.

[1] THIS JOURNAL, **42**, 226.
[2] *Ibid.*, **42**, 267.

The substances were intimately mixed in a two-liter balloon flask and heated to 200° in a bath of potassium sulphate and sulphuric acid. Carbon dioxide was passed into the flask during the heating to prevent oxidation. Large quantities of steam were evolved and the reacton proceeded just as smoothly as when the anhydride was used. The yield seemed to be as large and the product just as pure as that made from the anhydride, in fact, most of the tetrachlorgallein hydrate used by Mr. Briggs in this investigation was made by this method and purified by extracting the zinc chloride with methyl alcohol and crystallizing the residue from methyl alcohol.

An interesting experiment illustrating the sensitiveness of tetrachlorgallein to alkalies and the solubility of glass in water can be performed as follows: A very dilute solution of any form of tetrachlorgallein is used as indicator. Some finely powdered, easily fusible glass is placed in a test tube and washed with distilled water. Pure water, preferably conductivity water, containing no alkali is then added and a few drops of the indicator run in. In a few minutes the supernatant liquid and the powdered glass are colored an intense *purplish blue*, showing that the water has dissolved a certain quantity of alkali from the glass. Indeed, so sensitive is the tetrachlorgallein to alkalies that it has been found advisable to use Jena-glass flasks in working with solutions of the substance and to avoid the use of soft glass entirely. A solution of any form of tetrachlorgallein may also be used to show the alkalinity of the blood. If a drop of such a solution be placed on the skin, it turns first *red* and then, more slowly, blue, owing to the formation of sodium salts. If the spot be treated with acids, it turns red but soon becomes blue again after the acid is washed off.

SUMMARY

The results of this investigation may be briefly stated as follows:

1. Tetrachlorgallein combines with *two* molecules of acetone to form a *colorless* diacetonate. This loses acetone when

kept in a desiccator over phosphorus pentoxide and becomes *colored*, the color being deepest red when *one* molecule of acetone has evaporated. In the air, the diacetonate loses acetone and takes up water, turning red and forming the *colored* hydrate. A structural formula for the compound, in accord with these facts, has been suggested, page 10.

2. A *colorless* etherate of tetrachlorgallein has been made. This loses ether and takes up water when exposed to the air, forming a mixture of the *colorless* hydrate and the *colorless* carbinolcarboxylic acid. A structural formula, in accord with this conduct, has been suggested for the compound, page 17.

3. Anhydrous tetrachlorgallein absorbs hydrochloric acid gas very readily, forming a *red* hydrochloride, which, when heated to 157°, loses all its hydrochloric acid and goes back to the original tetrachlorgallein. Here again the transformation from the lactoid to the quinoid condition and back again takes place in *solids*.[1]

4. Two hydrates of tetrachlorgallein have been made, one *colorless* and the other *colored*. To the *colorless* product the *lactoid* formula has been assigned, while the *quinoid* formula best represents the conduct of the *red* modification.[2] The *red* hydrate takes up a molecule of hydrochloric acid, *without losing water*, to form the *hydrochloride of the hydrate*, while the *colorless* hydrate *loses a molecule of water* and takes up hydrochloric acid, forming the same *red* hydrochloride as the anhydrous tetrachlorgallein does, thus strikingly confirming the structural formulas given the two isomers. With ammonia both hydrates give the same tetrammonium salt as the anhydrous tetrachlorgallein does and both lose water, as the formulas require. Both hydrates, when heated, yield the same anhydrous tetrachlorgallein, which, from its slight color, is probably the lactoid modification (page 12).

5. A *colored* tetrammonium salt and also a *colored* monoammonium salt have been prepared from the *red* hydrate by the action of ammonia. The *colorless* hydrate gives the

[1] THIS JOURNAL, **42**, 256, 258 and 265.
[2] Page 30 and THIS JOURNAL, **42**, 255.

same *colored* tetrammonium salt when brought into contact with *dry* ammonia gas, again showing that the transformation of the *lactoid* into the *quinoid* condition can take place in *solids*.

6. Tetrachlorgalleincarbinolcarboxylic acid, a *colorless* compound, has been made and studied. It is formed when any form of tetrachlorgallein (the *colorless* hydrate, the *red* hydrate or the anhydrous product) or the diacetonate is dissolved in acetone or methyl alcohol and the solution poured into a large excess of acidified water. The anhydrous carbinol acid, obtained by heating the acid to constant weight at 158°, still contains one molecule of water (of constitution) more than the anhydrous tetrachlorgallein and it retains this water even when heated to 203°. Yet it combines *very readily, even in the cold*, with *dry* hydrochloric acid to form the *red* hydrochloride and with *dry* ammonia to form the *colored* tetrammonium salt and *at the same time loses a molecule of water*. This confirms, in a very striking manner, Baeyer's statement that *all carbinols are colorless and that color only appears in consequence of the loss of water*.

7. A *colored* monopotassium salt of tetrachlorgallein has been made from the *colorless* carbinol acid. Here again a molecule of water splits off from the carbinol acid in the formation of this *colored* salt.

8. The *colorless* carbinol acid splits off a molecule of water also when heated with acetic anhydride, forming the *colorless* tetrachlorgallein tetracetate, a lactoid compound, thus showing that the elimination of water from the carbinol acid does not necessarily give a *colored* compound. The product resulting from the loss of water must have the *quinoid structure* in order that a *colored* compound may be formed.

9. A simpler method for the preparation of tetrachlorgallein hydrate, involving the use of tetrachlorphthalic acid instead of the anhydride, has been found.

CORNELL UNIVERSITY,
May, 1911

A STUDY OF THE CONDUCTIVITY AND DISSOCIATION OF ORGANIC ACIDS IN AQUEOUS SOLUTION BETWEEN ZERO AND THIRTY-FIVE DEGREES

By E. P. Wightman and Harry C. Jones

HISTORICAL

White and Jones,[1] in their work on the conductivity and dissociation of organic acids in aqueous solution, give a survey of the data obtained up to that time, and a large amount of the earlier work is discussed in full. It is not necessary to repeat all of this discussion, but a short summary of the results as a whole will be given as an introduction to this work.

One of the first things noticed by early workers was the increase in molecular conductivity with rise in temperature and increasing dilution. It was shown also that this increase is, for most electrolytes in dilute solutions, a parabolic function of the temperature, and the following interpolation formula was deduced and employed by Euler:[2]

$$\lambda = a + bt - ct^2$$

in which λ is the molecular conductivity at the temperature t, a is the known conductivity at some other temperature, and b and c are constants depending upon the nature of the electrolytes. Extensive use has been made of this formula.

As the dilution increases the rate of increase in conductivity becomes less, and in some cases there is a maximum value of conductivity, as was shown by Grotian,[3] Jahn,[4] Schaller,[5] and the later workers. As a matter of fact, the maximum occurs for nearly all strong electrolytes at dilutions at which the conductivity can be measured directly.

This is not the case with most of the organic acids, but indirect methods were devised by Ostwald[6] and by White

[1] This Journal, **44**, 159 (1910).
[2] Z. physik. Chem., **21**, 257 (1896).
[3] Pogg. Ann., **154**, 215 (1875).
[4] Z. physik. Chem., **18**, 72 (1895).
[5] *Ibid.*, **25**, 497 (1898).
[6] *Ibid.*, **1**, 74, 97 (1887); **2**, 840 (1888).

and Jones,[1] based upon Kohlrausch's law of the independent migration velocities of ions, by means of which μ_∞ for the acids could be determined.

Ostwald showed that there is a constant difference between μ_v for a given dilution, say thirty-second normal, of the sodium salt of any acid, and the μ_∞ value of the same, which is found at about ten hundred and twenty-fourth normal. By means of this constant difference he calculated the μ_∞ values of a large number of sodium salts without direct measurement, and from these it was easy to determine the μ_∞ values of the acids in question, by subtracting the value for the migration velocity of the sodium ion, and adding the corresponding constant for hydrogen.

A second method suggested by Ostwald was based upon the fact that the velocities of anions of acids containing over twelve atoms in the anion are dependent upon the number of these atoms present—ions with the largest number of atoms having the smallest velocity.

The method of White and Jones (for monobasic acids) is based upon the direct measurement of the μ_∞ value of the sodium salt of the acid and will be discussed later. The μ_∞ values of the dibasic acids were determined by a graphic method similar to the second method used by Ostwald.

Just as the molecular conductivity increases at a diminishing rate with dilution, so also it increases at a diminishing rate with rise in temperature, as was brought out by Schaller[2] and by Noyes.[3]

Another important fact is the decrease in dissociation with rise in temperature, first noticed by Arrhenius[4] in the case of phosphoric and hypophosphoric acids, later brought out by Schaller[5] and a number of others,[6] and finally thoroughly

[1] THIS JOURNAL, **44**, 159 (1910).
[2] Z. physik. Chem., **25**, 497 (1898).
[3] J. Am. Chem. Soc., **26**, 134 (1904); **30**, 335 (1908); **31**, 987 (1909).
[4] Z. physik. Chem., **4**, 96 (1889).
[5] *Ibid.*, **25**, 497 (1898).
[6] Jones and West: THIS JOURNAL, **34**, 357 (1905); Jones and Jacobson: *Ibid.*, **40**, 355 (1908); Jones and Clover; *Ibid.*, **43**, 187 (1910); White and Jones: *Ibid.*, **44**, 159 (1910).

established by the work of Noyes[1] at higher temperatures. No entirely satisfactory explanation of this decrease in dissociation has been given; but the results of Noyes in his first work[2] show that the dissociations of the two salts, sodium chloride and potassium chloride, are nearly identical at all temperatures and concentrations; and he says: "This gives support to the idea that decrease of conductivity and of calculated dissociation with rise in temperature is due to a physical cause (probably in some way to the electrical charges on the ions) and not to specific chemical affinity." More will be said about this in another connection.

It was pointed out by the later workers (Schaller[3] was one of the first) that the temperature coefficients of conductivity increase with dilution and decrease with rise in temperature for acids, and increase with temperature for neutral salts. Amino acids are an exception to this, as was shown by White and Jones.[4] They explain the increase with rise in temperature as "probably due to the formation of inner salts having both acidic and basic groups, which break up with rise in temperature." The decrease of the temperature coefficients for nearly all other acids is explained by them in terms of the theory of hydration.[5]

It was found by White and Jones that the Ostwald dilution law[6] holds very well for dilute, weak organic acids, with the exception of the amino acids. The law is expressed thus:

$$\frac{\alpha^2}{(1-\alpha)V} = K$$

where $\alpha = \frac{\mu_v}{\mu_\infty}$ is the dissociation, V is the volume, and K is a constant. The law is easily deduced from the gas laws and those of osmotic pressure. The discrepancies in the temperature coefficients in the case of amino acids were explained as stated above, viz., as due to the breaking down of the inner salts.

[1] J. Am. Chem. Soc., **26**, 134 (1904); **30**, 355 (1908); **31**, 987 (1909).
[2] *Ibid.*, **26**, 134 (1904).
[3] Z. physik. Chem., **25**, 497 (1898).
[4] THIS JOURNAL, **44**, 159 (1910).
[5] *Ibid.*, **40**, 402 (1908).
[6] Z. physik. Chem., **2**, 36 (1888); **3**, 170 (1889). Jahn: *Ibid.*, **23**, 545 (1900).

Strong acids (and also other strong electrolytes) do not conform to the Ostwald law, and a large number of empirical formulae have been suggested,[1] all of which hold fairly well for specific cases, but only a few of which are of general application. These are discussed very thoroughly by Noyes,[2] who says of the following formulae:

$$\frac{\Delta_0 - \Delta}{C^{1/3}} = K \text{ (Kohlrausch)}$$

$$\frac{\Delta_0 - \Delta}{\Delta^{1/3} C^{1/3}} = K \text{ (Barmwater)}$$

$$\frac{\Delta_0 - \Delta}{\Delta^{3/2} C^{1/2}} = K \text{ (Van't Hoff)}$$

$$\frac{\Delta_0 - \Delta}{\Delta^2 C^{1/2}} = K \text{ (Rudolphi)}$$

"The Kohlrausch formula expresses the results for both salts (potassium and sodium chlorides) at all temperatures without great error, and the same is true of the Barmwater formula except at the highest temperature, where the deviation with both salts is large. The van't Hoff and Rudolphi formulas do not accord at all with the observed values at 306°, the deviations in the case of the latter being especially large; while at the lower temperatures, 140°, 218° and 281°, the van't Hoff formula is far less satisfactory than those of Kohlrausch and Barmwater. On the whole, therefore, the simple Kohlrausch formula furnishes the best representation of the results and the Barmwater next best."

In terms of the Ostwald formula, i. e., using the same notation, these would be:

$$\frac{1 - \alpha}{\sqrt[3]{1/V}} = K \text{ (Kohlrausch)}$$

$$\frac{1 - \alpha}{\sqrt[3]{\alpha/V}} = K \text{ (Barmwater)}$$

[1] Wied Ann., **26,** 200 (1885); **50,** 394 (1893). MacGregory: *Ibid.*, **51,** 133 (1894). Barmwater: Z. physik. Chem., **38,** 134, 428 (1899). Sabat: *Ibid.*, **41,** 224 (1902). Müller: Compt. rend., **128,** 505 (1899). Kohlrausch: Sitz. preus. Akad., **44,** 1002 (1900). Rudolphi: Z. physik. Chem., **17,** 385 (1895). Van't Hoff: *Ibid.*, **18,** 300 (1895). Kohlrausch: *Ibid.*, **18,** 662 (1895). Storch: *Ibid.*, **19,** 13 (1896). Bancroft: *Ibid.*, **31,** 188 (1899). Jahn: *Ibid.*, **37,** 499 (1901); **41,** 265, 288 (1902). Nernst: *Ibid.*, **38,** 493 (1901).

[2] J. Am. Chem. Soc., **26,** 162 (1904).

Noyes[1] says also, concerning strong electrolytes: "This principle has now received a further confirmation through the demonstration of the fact that certain purely empirical laws relating to the ionization of salts in water still continue to be valid, even when the physical condition of that solvent is greatly altered by a large change in the temperature. This principle is that the ionization of salts, strong acids and bases is a phenomenon primarily determined not by specific chemical affinities, but by electrical forces arising from charges on the ions; that it is not affected (except in a secondary degree) by chemical mass action, but is regulated by certain general, comparatively simple laws, fairly well established empirically but of unknown theoretical significance, and that, therefore, it is a phenomenon quite distinct in almost all its respects from the phenomenon of dissociation ordinarily exhibited by chemical substances, including that of the ionization of weak acids and bases."

He distinguishes between ordinary unchanged molecules, which he calls "chemical molecules," and a loosely united ionized molecule, or "electrical molecule."

Walden[2] in 1891 and 1892 showed, in his work on di-, tri-, and tetracarboxylic acids, that the general tendency of such organic acids is to dissociate, up to quite high dilutions, like monobasic acids. In the case of tribasic acids he mentions the three possibilities:

$$A'''H_3 = A'''H_2 + H \qquad (1)$$
$$A'''H_3 = A'''H + H + H \qquad (2)$$
$$A'''H_3 = A''' + H + H + H \qquad (3)$$

of which only the first takes place at ordinary dilutions.

The same thing was found to be the case by Walker,[3] namely, that dibasic acids behave just like monobasic acids within the limits of dilutions at which he worked. Pimelic acid, for instance, splits into $\overset{+}{H}$ and $\overset{-}{O}OC(CH_2)_5COOH$, and not into $\overset{+}{H}$, $\overset{+}{H}$, and $\overset{=}{O}OC(CH_2)_5COO$.

[1] J. Am. Chem. Soc., **30**, 335 (1908).
[2] Z. physik. Chem., **8**, 434 (1891); **10**, 563 (1892).
[3] J. Chem. Soc., **61**, 696 (1892).

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EXPERIMENTAL

Apparatus

Burettes and flasks (200 cc., 250 cc., 500 cc., and 1000 cc.) were all calibrated by the method of Morse and Blalock[1] for a temperature of 20°. The 200 cc. flasks were also calibrated by weight, and the results were found to agree very closely. The time necessary to drain all pipettes and burettes was determined and properly taken into account in the measurements. The thermometers were also carefully standardized against a Reichsanstalt thermometer.

At first a Wheatstone bridge was used for making the conductivity measurements, and this was calibrated by the method of Strouhal and Barus.[2] Later a very fine Kohlrausch slide-wire bridge was obtained, by means of which it was possible to read distances on the slide-wire corresponding to tenths of a millimeter (the total length of the wire was five meters).

The resistance box employed in the later work was one that had been standardized by the U. S. Bureau of Standards. The one first used was later compared with this one, and was found to be accurate to well within the limits of experimental error.

Three thermostats were employed to keep the cells at constant temperature; one for 0°, similar to that described by Jones and Jacobson;[3] one for 15° and 25°, a galvanized tub containing 25 or 30 liters of water, and in the bottom of which was placed a lead coil through which cold water was passed under constant pressure; a third for 35°, differing from the latter only in not having a coil in the bottom. They were both kept constantly stirred by propellers driven by a hot-air engine. In this way it was possible to keep the temperature constant to within 0°.02.

At first the thermostats were regulated by hand, and this was found to be sufficient, provided they were continually watched. It was found, however, that thermoregulators save both time and labor, so that finally these were installed.

[1] THIS JOURNAL, **16**, 479.

[2] Wied. Ann., **10**, 326. Kohlrausch and Holborn: "Leitvermögen der Electrolyte," p. 45 (1898).

[3] THIS JOURNAL, **40**, 355 (1908).

They were of the general type used in this laboratory, so need not be described here.

The cells resembled those used by Jones and Bingham,[1] with platinum-plate electrodes, attached to glass tubes containing mercury, the tubes being sealed into ground-glass stoppers. As many as eight cells were employed with constants ranging from about 330 to about 10 in Siemens' units. A cell of special type,[2] having a very low constant, was used for obtaining the conductivity of the water.

In order to get a sharp reading in the cells, electrodes were covered with a fine coating of platinum black in the usual manner.

Mention only will be made of the viscosity apparatus, which was of the form used for such work in this laboratory,[3] consisting of a picnometer, viscometer, and a stopwatch.

Reagents

Water for making up all solutions and for the final purification of the acids was obtained by the method of Jones and Mackay.[4]

Standard Acid.—Two methods were made use of for standardizing sulphuric acid; namely, the barium sulphate method, and a check method which consists in standardizing against a solution of sodium hydroxide, which, in turn, has been titrated against very thoroughly standardized hydrochloric acid. Both methods gave practically identical results.

As to the first one, the acid was made up to approximate strength (about 0.15 N) from pure concentrated sulphuric acid. Three 50 cc. portions of the dilute solution were then run into fairly large beakers and further diluted, and then heated nearly to boiling. A hot, dilute solution of barium chloride, containing a slight excess of the salt, was then poured gradually down the side of one of the beakers containing sulphuric acid, to which had been added a few drops of hydrochloric acid, and which was kept stirred all the while.

[1] THIS JOURNAL, **34**, 493 (1905).

[2] *Ibid.*, **45**, 282 (1911).

[3] Ostwald-Luther: Physik.-chem. Mess., 2nd Ed., p. 260. Z. physik. Chem., **61**, 651 (1908).

[4] THIS JOURNAL, **19**, 91. Z. physik. Chem., **22**, 237.

In this way a complete precipitation takes place almost at once. Nevertheless, the beakers were allowed to stand on a warm sand bath for half an hour. The precipitate was collected in a Gooch crucible on a layer of purified asbestos.

Standard Alkali.—In order to be able to use the sodium hydroxide both for titration purposes and for preparing the sodium salt solutions of the acids, it was necessary to have an aqueous solution of the alkali, as free as possible from carbonates and other impurities. To prepare such a solution the method of H. W. Cowles, Jr.,[1] is an excellent one.

One hundered grams of sodium hydroxide, purified from alcohol, was dissolved in 100 grams of conductivity water (obtained as above described) and the concentrated solution was allowed to stand in a closed vessel for about a week. By that time practically all the carbonate, etc., was precipitated and there was left a perfectly clear supernatant solution of sodium hydroxide, portions of which were pipetted out and diluted to the proper strength with conductivity water. The dilute solution was then standardized by means of the standard sulphuric acid, and otherwise. When thus prepared, the solution is perfectly free from carbonate, as is shown by the fact that it does not give a precipitate of barium carbonate with barium hydroxide, and that when titrated with indicators, both those that are sensitive and those that are not sensitive to carbonates, the results are practically the same.

Organic Acids.—Kahlbaum's so-called pure acids were almost exclusively employed, and before using them they were all still further purified by one method or another, according to the nature of the acid. Their purity was tested by means of their melting or boiling points, and by titration. No acids were used whose purity could not thus be established.

Sodium Salts of Organic Acids.—These salts, for the most part, were prepared by titrating a solution of the acid (usually about N/128) with a standard solution of sodium hydroxide exactly to neutrality, using a drop of phenolphthaleïn as indicator. Alizarin is also a good indicator and was used in later work because it is less sensitive to carbonic acid.

[1] J. Am. Chem. Soc., **30**, 1192 (1908).

In a few cases the purified sodium salts were weighed out and made up to the proper strength.

The potassium chloride used for obtaining cell constants was Kahlbaum's purest. To insure its purity it was precipitated from a saturated solution by hydrochloric acid, and then recrystallized three times from conductivity water. Finally, after drying in an oven for some time, it was heated at a moderate temperature for ten or fifteen minutes in a porcelain dish over a Bunsen flame.

Procedure

The molecular conductivities and temperature coefficients were calculated in the usual manner.

For percentage temperature coefficients Schaller's[1] equation,

$$\beta = \frac{\mu_{t_1} - \mu_t}{\mu_{t_1}(t_1 - t)}$$

was employed.

The equations given above for dissociation and for dissociation constants

$$\alpha = \frac{\mu_v}{\mu_\infty} \text{ and } K = \frac{\alpha^2}{(1 - \alpha)V}$$

were employed in calculating these values for weak monobasic acids. Constants for the strong acids were calculated by a method which will be described later.

Cell Constants.—The usual method, already described by White and Jones,[2] was followed, a 0.02 N solution of potassium chloride being used for the cells in which the electrodes were fairly wide apart, and a 0.002 N solution for those with the platinum plates close together. The value $\mu_{50} = 129.7$ for the conductivity of the 0.02 N solution at 25° was taken from Kohlrausch, and the value $\mu_{500} = 137.9$ for the 0.002 N solution was found by direct measurement.

The cells were standardized about once a month, but very little change in the constants was found to take place, even in the course of the whole year. Great care was always taken not to change the position of the electrodes, which would of course alter the values of the constants. The following table

[1] Z. physik. Chem., **2**, 561 (1888).

[2] This Journal, **42**, 527 (1909).

is typical of the manner in which the results were tabulated, W being the resistance in the rheostat, b the distance on the wire from the point of contact to one end of the wire, and K the cell constants.

Table I.—Cell Constants

Cell	Solution	W	b	K	Mean
VIII	0.02 N	100	559.0	328.82	328.82
		140	475.2	328.84	
		150	458.0	328.80	
VII	0.02 N	80	471.3	184.99	184.97
		84	459.1	184.94	
		88	447.6	184.97	
VI	0.02 N	60	458.0	131.52	131.52
		63	445.9	131.52	
		66	434.5	131.54	
V	0.02 N	40	454.3	86.38	86.38
		42	442.2	88.37	
		44	430.8	86.40	
IV	0.02 N	30	481.6	72.30	72.30
		32	465.5	72.30	
		34	450.4	72.24	
III	0.002 N	200	445.0	44.10	44.10
		210	433.0	44.10	
		220	421.6	44.10	
II	0.002 N	100	443.7	21.94	21.94
		110	420.5	21.95	
		120	469.9	21.94	
I	0.002 N	40	505.6	11.240	11.243
		46	470.5	11.241	
		48	460.0	11.245	
A	0.0005 N	40	451.0	2.381	2.381
		42	439.0	2.381	
		44	427.5	2.381	
V	0.002 N	250	555.7	138.68	
		260	546.0	138.67	
		270	536.5	138.75	
IV	0.002 N	250	511.2	138.66	138.66
		260	501.5	138.60	
		270	492.0	138.64	
II	0.0005 N	340	473.4	143.49	
		350	466.0	143.64	
		370	452.3	143.46	
I	0.0005 N	160	495.0	143.39	143.44
		170	479.9	143.41	
		180	465.6	143.39	

Three readings were taken for each cell, and these agree to within two or three hundredths of a per cent. All the later work, in which the Kohlrausch slide-wire bridge was used, was equally as accurate. In one case cell constants were taken two days in succession, using entirely new solutions on the second day, and here again the agreement was practically perfect.

μ_∞ *for the Sodium Salts of Organic Acids*

Whenever it was possible, the μ_∞ values were obtained by direct measurement, as was done by White and Jones. Such values are given in the following table:

Table II.—μ_∞ for Sodium Salts

Sodium Trichloracetate

V	0°	15°	25°	35°
1024	41.96	64.75	82.45	101.98

$K_t = 41.96 + 1.38t + 0.00952t^2$

Sodium Cyanacetate

V	0°	15°	25°	35°
2048	44.65	65.43	86.80	106.0

$K_t = 44.65 + 1.52t + 0.00668t^2$

Sodium α-Brompropionate

V	0°	15°	25°	35°
1024	42.10	65.04	84.26	105.4
2048	44.94*	69.83	89.61*	108.2*
4096	46.63	70.38	90.40	111.2

$K_t = 44.94 + 1.74t + 0.002t^2$

Sodium α,β-Dibrompropionate

V	0°	15°	25°	35°
2048	41.56	64.89	83.24	103.08

$K_t = 41.56 + 1.44t + 0.009t^2$

Sodium β-Iodpropionate

V	0°	15°	25°	35°
2048	41.54	63.70	81.16	102.8

$K_t = 41.54 + 1.18t + 0.0168t^2$

Sodium Levulinate

V	0°	15°	25°	35°
2048	38.47	59.11	75.13	92.94

$K_t = 38.47 + 1.242t + 0.00898t^2$

Sodium α-Brombutyrate

V	0°	15°	25°	35°
1024	41.50	64.16	81.90	101.0
2048	42.46*	65.07	82.53*	102.6*
4096	43.34	66.33	84.32	103.4

$K_t = 42.46 + 1.32t + 0.0115t^2$

Sodium Hydroxyisobutyrate

V	0°	15°	25°	35°
2048	40.44	62.36	79.42	97.74

$K_t = 40.44 + 1.36t + 0.00779t^2$

Sodium Isovalerate

V	0°	15°	25°	35°
2048	32.31	50.15	63.87	79.33

$K_t = 32.31 + 1.06t + 0.0081t^2$

Sodium Caprylate

V	0°	15°	25°	35°
2048	42.67	61.85	77.61	95.77

$K_t = 42.67 + 1.099t + 0.0120t^2$

Sodium Benzilate

V	0°	12°	25°	35°
1024	35.1	50.5	69.5	86.2
2048	36.3	52.2	71.5	88.9
4096	35.8	51.7	70.8	88.1

$K_t = 36.3 + 1.17t + 0.0095t^2$

Sodium Chlorbenzoate

V	0°	15°	25°	35°
2048	38.03	58.97	75.47	93.18

$K_t = 38.03 + 1.30t + 0.0078t^2$

Sodium p-*Nitrobenzoate.*

V	0°	12°	25°	35°
1024	38.85	55.48	75.71	93.30
2048	39.78	56.28	76.48	95.80
4096	38.91	55.01	75.86	94.00

$K_t = 39.78 + 1.14t + 0.0133t^2$

Sodium 1,2,4-Dinitrobenzoate

V	0°	15°	25°	35°	
2048	37.80	58.25	74.77	92.90	(by titration)
				92.83	(from dry salt)

$K_t = 37.80 + 1.24t + 0.0095t^2$

Sodium 1,3,5-Dinitrobenzoate

V	0°	15°	25°	35°	
2048	37.83	58.30	74.60	92.93	(by titration)

$$K_t = 37.83 + 1.24t + 0.0095t^2$$

Sodium 1,3,5-Dinitrobenzoate

V	0°	15°	25°	35°	
1024	36.74	56.53	71.81	87.70	(solution of dry salt)
2048	37.46	57.56	73.13	89.64	
4096	37.98	58.10	74.60	91.70	

Sodium 1,2,4-Dihydroxybenzoate

V	0°	15°	25°	35°
2048	39.64	60.72	77.49	95.11

$$K_t = 39.64 + 1.337t + 0.00708t^2$$

Sodium 1,2,5-Dihydroxybenzoate

V	0°	15°	25°	35°
2048	39.36	60.58	77.52	95.62

$$K_t = 39.36 + 1.324t + 0.0081t^2$$

Sodium p-*Sulphamidobenzoate*

V	0°	15°	25°	35°
2048	39.30	60.23	76.57	94.00

$$K_t = 39.30 + 1.31t + 0.0072t^2$$

In nearly every one of the above cases a concentration of N/2048 alone was used, since it was found by White and Jones that the μ_∞ values of the sodium salts generally occur at this concentration.

The fact that the conductivity of a salt made up by titration and that of the same salt made up from the dry solid agree shows that the titration method is reliable.

It is seen, as would be expected from previous work, that the μ_∞ values of the sodium salts of isomeric acids are practically identical, as, for example, sodium 1,2,4- and 1,3,5-dinitrobenzoates, and sodium 1,2,4- and 1,2,5-dihydroxybenzoates.

Further, the μ_∞ values of the strong acids calculated from the sodium salts are identical with the maximum values of the acids themselves. Trichloracetic and 1,2,4-dinitrobenzoic acids are examples illustrating this point.

Moreover, we see from the tables that those salts with the largest number of atoms in the anion have the highest μ_∞ values. The curves expressing the μ_∞ values for these acids bring this point out still more strikingly.

μ_∞ *Values of the Acids*

The method by which these values are calculated has already been referred to. Essentially, it is merely a subtracting of the migration velocity value of the sodium ion from the μ_∞ value of the sodium salt, and an addition of the migration velocity value of the hydrogen ion. In actual practice, the following equation was used:

$$\mu_\infty \text{ (acid)} = \mu_\infty \text{ (HCl)} + \mu_\infty \text{ (Na salt of acid)} - \mu_\infty \text{ (NaCl)}$$

As the values of conductivity between 0° and 25° were, throughout the present work, obtained almost exclusively at 15°, the equations given by White and Jones for calculating the μ_∞ values of sodium chloride and of hydrochloric acid were made use of in order to obtain the μ_∞ values of the acids worked with at this temperature.

For sodium chloride at 15°,

$$\mu_\infty = (63.04 + 2.04t + 0.00823t^2) = 95.49$$

and for hydrochloric acid at 15°,

$$\mu_\infty = (245.4 + 6.06t - 0.00776t^2) = 334.5$$

In the table given below are presented the μ_∞ values of all the acids with which we worked (except dichlorphthalic, tetrachlorphthalic, and meconic acids).

The values for the acids marked with an asterisk were not obtained by means of the method stated above, since they are dibasic and their sodium salts do not yield a maximum value of conductivity at any dilution up to N/4096, which is the highest dilution with which we worked.

A curve, in which the ordinates represent μ_∞ values and abscissas the number of atoms, was plotted for a large number of monobasic acids, and by placing the dibasic acids in their

proper position on this curve (according to the number of atoms present) their μ_∞ values can be obtained (see Fig. I).

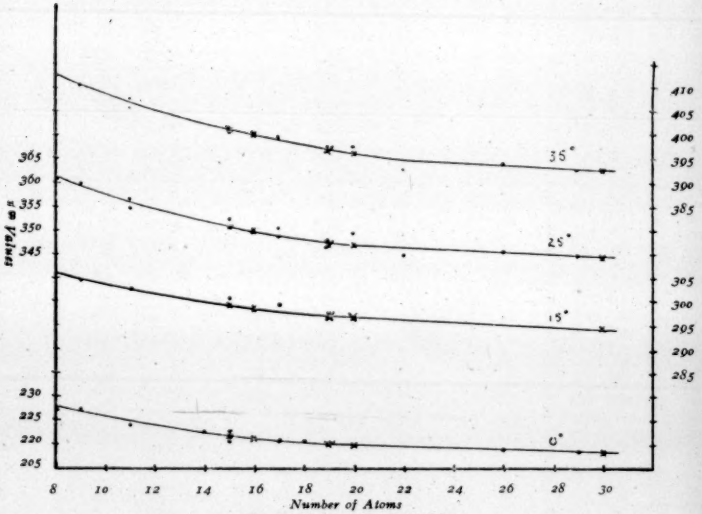

Fig. I—Limiting Conductivities

Table III.—μ_∞ Values of the Acids

Acid	μ_∞ 0°	μ_∞ 12°	μ_∞ 15°	μ_∞ 25°	μ_∞ 35°
Trichloracetic	224.8	...	303.9	355.9	406.4
Cyanacetic	271.1	...	304.5	360.0	410.0
Benzilic	218.7	280.5	...	344.7	392.9
α-Brompropionic	229.0	...	308.9	363.6	415.2
α,β-Dibrompropionic	223.9	...	303.9	356.4	407.0
β-Iodpropionic	223.9	...	302.8	354.4	406.8
Levulinic	220.9	...	298.2	348.3	396.9
α-Brombutyric	230.7	...	304.1	357.5	407.4
Hydroxyisobutyric	222.8	...	301.4	352.6	401.7
Isovaleric	214.7	...	289.2	337.1	383.3
Caprylic	225.1	...	300.9	350.8	399.8
l-Tartaric*	221.0	...	298.8	350.0	399.9
Thiodiglycolic*	221.6	...	300.2	351.1	401.0

Table III.—(Continued)

Acid	μ_∞ 0°	μ_∞ 12°	μ_∞ 15°	μ_∞ 25°	μ_∞ 35°
Tricarballylic*	219.9	...	296.7	347.6	396.8
p-Nitrobenzoic	222.2	284.6	...	349.7	399.8
1,2,4-Dinitrobenzoic	200.0	...	297.3	347.9	396.8
1,3,5-Dinitrobenzoic	220.2	...	297.4	347.4	396.9
o-Chlorbenzoic	220.4	...	301.8	348.7	397.2
1,2,4-Dihydroxybenzoic	222.0	...	299.8	350.7	399.1
1,2,5-Dihydroxybenzoic	221.8	...	299.6	350.7	399.6
p-Sulphamidobenzoic	221.7	...	299.3	349.8	398.0
Benzenesulphonic	228.0	...	309.0	359.0	410.3
p-Toluenesulphonic	210.6	269.7	...	332.7	379.3
m-Nitrobenzenesulphonic	204.5	...	16° 275.5	223.5	369.4
1,2,4-Nitrotoluenesulphonic	200.5	...	276.5	318.4	361.9
Camphoric*	218.3	279.8	...	344.5	392.5
Uric*	221.0	...	298.8	350.0	399.9
Cyanuric	...	...	...	...	405.0

RESULTS

Trichloracetic Acid, CCl_3COOH

The acid is very hygroscopic, so it was not dried thoroughly after recrystallization from water, but was made up to approximate strength and then standardized by titration.

Ostwald[1] determined the conductivity of the acid at 25° and comparison of his results with our own at the same temperature shows a fairly close agreement, especially at the higher dilutions:

	Ostwald	From Tables IV and VI
V	μ_V 25°	μ_V 25°
32	323.0	322.46
128	341.0	344.90
512	353.7	353.96
1024	356.0	355.94

The relation of trichloracetic acid to acetic acid, monochloracetic acid, and other acetic acid derivatives, was brought out with sufficient clearness by Ostwald, and need not be discussed here. The acid itself, however, is of especial interest, because it is a very strong electrolyte (very nearly as strong as hydrochloric acid).

We see from Table VI that the acid is entirely dissociated at N/2048. The μ_∞ value ($\mu_\infty = 358$) given by Ostwald

[1] Z. physik. Chem., **3**, 177 (1889).

is greater than any of the conductivity values given by him, and, therefore, his percentage dissociation values do not reach a maximum; but we find that μ_∞, as obtained from the sodium salt, agrees very closely with the maximum value for conductivity of the acid at 25° (at N/2048).

Table IV.—Molecular Conductivity

V	0°	15°	25°	35°
8	193.02	256.24	298.40	334.67
32	208.75	277.67	322.46	363.69
128	221.73	297.62	344.90	389.83
512	223.65	302.33	353.96	403.45
1024	224.77	303.94	355.94	406.44
2048	221.52	300.21	349.57	397.46

Table V.—Temperature Coefficients

	0°–15°		15°–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	4.25	2.20	4.22	1.65	3.63	1.22
32	4.60	2.20	4.48	1.61	4.12	1.28
128	5.06	2.28	4.73	1.59	4.49	1.30
512	5.25	2.35	5.16	1.70	4.95	1.40
1024	5.28	2.35	5.20	1.71	5.05	1.42
2048	5.24	2.37	4.94	1.65	4.79	1.37

μ_∞ *Values (measured directly)*

V	0°	15°	25°	35°
1024	224.77	303.94	355.94	406.44

μ_∞ *Values (from sodium salt)*

V	0°	15°	25°	35°
1024	223.67	303.86	355.65	405.91

Table VI.—Percentage Dissociation

V	0°	15°	25°	35°
8	85.87	84.31	83.83	82.34
32	92.87	91.36	90.59	89.88
128	98.65	97.92	96.90	95.91
312	99.50	99.47	99.44	99.26
1024	100.00	100.00	100.00	100.00

Cyanacetic Acid, $CH_2(CN)COOH$

The acid was easily purified by recrystallization from water, and was dried over sulphuric acid in a vacuum desiccator. The pure, dry acid has a melting point of 65°.

It is of interest to note the effect of the cyanogen group when introduced into acetic acid, and also to compare its effect with that of other groups.

	Acetic Acid White and Jones[1]		*Monochloracetic Acid* Ostwald[2]		*Monobromacetic Acid* Ostwald[2]	
V	μ_v 25°	α 25°	μ_v 25°	α 25°	μ_v 25°	α 25°
8	4.342	1.20	...	...	...	...
32	8.699	2.41	72.4	19.94	68.7	18.95
128	17.11	4.74	127.7	35.2	122.3	33.7
512	33.24	9.21	205.8	56.8	199.2	55.0
1024	45.87	12.71	249.2	68.7	241.2	66.6
2048	63.00	17.45	...	...	...	...
	$K^3 = 0.184$		$K = 15.5$		$K = 13.8$	

	Phenylacetic Acid White and Jones[4]		*Cyanacetic Acid* From Tables VII and IX	
V	μ_v 25°	α 25°	μ_v 25°	α 25°
8	...	...	59.53	16.54
32	14.15	4.05	106.47	29.58
128	27.96	8.01	178.86	49.68
512	52.39	14.97	259.64	72.12
1024	71.63	20.52	291.56	80.99
2048	95.50	27.36	314.3	87.30
	$K = 0.545$		$K = 36.3$	

The strong negative character and influence of the cyanogen group is strongly brought out by the fact that the constant for cyanacetic acid is but little less than that for monobromacetic acid, and that it is very nearly two hundred times as great as that for acetic acid.

Table VII.—Molecular Conductivity

V	0°	15°	25°	35°
8	38.27	51.66	59.53	66.15
32	68.70	92.26	106.47	118.79
128	114.23	154.10	178.86	199.67
512	164.90	223.37	259.64	293.00
1024	187.49	252.59	291.56	332.00
2048	199.90	270.40	314.30	356.60

[1] THIS JOURNAL, **44**, 165 (1910).

[2] Z. physik. Chem., **3**, 178 (1889).

[3] NOTE.—K, throughout this work, means *constant* $\times 10^4$.

[4] THIS JOURNAL, **44**, 168 (1910).

Table VIII.—Temperature Coefficients

	0°–15°		15°–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	0.893	2.33	0.787	1.52	0.662	1.11
32	1.67	2.29	1.42	1.54	1.23	1.16
128	2.66	2.33	2.48	1.61	2.08	1.16
512	3.90	2.36	3.63	1.62	3.04	1.17
1024	4.35	2.32	3.97	1.57	4.04	1.39
2048	4.70	2.35	4.39	1.62	4.23	1.35

Table IX.—Percentage Dissociation

V	0°	15°	25°	35°
8	16.86	16.97	16.54	16.13
32	30.26	30.30	29.58	28.97
128	50.31	50.60	49.68	48.70
512	72.63	73.36	72.12	71.46
1024	82.58	82.96	80.99	80.98
2048	88.04	88.80	87.30	86.97

Table X.—Dissociation Constants $\times 10^4$

V	0°	15°	25°	35°
8	43	42	41	39
32	41	40	39	37
128	40	39	38	36
512	38	37	36	35
1024	38	36	35	34
2048	32	31	29	28

Benzilic or Diphenylglycolic Acid, $(C_6H_5)_2C(OH)COOH$

The ordinary method of recrystallization was used for purifying this acid (melting point, 150°).

Here we have the effect of both hydroxyl and phenyl groups, and the result is an acid ($K_{25°} = 9.20$) which is fifty times as strong as acetic acid ($K_{25°} = 0.184$)[1] and six times as strong as glycolic acid ($K_{25°} = 1.52$).[2]

Table XI.—Molecular Conductivity

V	0°	12°	25°	35°
128	63.8	81.7	101.5	115.0
512	106.4	138.3	169.5	186.9
1024	133.6	169.8	208.4	237.1
2048	152.3	193.0	233.7	260.6

[1] THIS JOURNAL, **44**, 168 (1910).

[2] Ostwald: Z. physik. Chem., **3**, 183 (1889).

Table XII.—Temperature Coefficients

	0°–12°		12°–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
128	1.52	2.38	1.50	1.84	1.35	0.93
512	2.66	2.50	2.24	1.62	1.94	1.04
1024	3.02	2.26	2.97	1.75	2.87	1.23
2048	3.39	2.23	3.13	1.62	2.69	1.03

Table XIII.—Percentage Dissociation

V	0°	12°	25°	35°
128	29.17	29.08	29.45	29.27
512	48.64	49.24	48.60	47.57
1024	61.08	60.44	60.46	60.20
2048	69.63	68.71	67.81	64.82

Table XIV.—Dissociation Constants $\times 10^4$

V	0°	12°	25°	35°
128	9.38	9.10	9.60	9.46
512	9.00	9.32	8.97	8.43
1024	9.36	9.02	9.02	8.89
2048	7.80	7.37	6.97	5.83

α-Brompropionic Acid, $CH_3.CHBr.COOH$

The acid was purified by distillation and was then a clear colorless liquid, boiling at 205°. The calculated quantity for making up a N/32 solution was accurately weighed out into a weighing bottle and then poured into a flask and diluted. A portion of this dilute solution, enough to make a N/1024 solution, was titrated in order to form the sodium salt, and also to be sure of its normality.

Table XV.—Molecular Conductivity

V	0°	15°	25°	35°
32	38.00	49.38	58.86	61.5
128	77.10	100.00	114.4	125.9
512	124.7	164.1	186.8	206.7
1024	151.7	200.8	229.5	257.0
2048	171.5	227.4	262.0	295.3

Table XVI.—Temperature Coefficients

	0°–15°		15°–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
32	0.76	2.00	0.65	1.31	0.56	1.00
128	1.53	1.99	1.44	1.44	1.05	0.92
512	2.63	2.11	2.27	1.38	1.99	1.07
1024	3.27	2.16	2.87	1.43	2.75	1.17
2048	3.70	2.16	3.46	1.52	3.33	1.27

Table XVII.—Percentage Dissociation

V	0°	15°	25°	35°
32	16.60	15.99	15.38	14.81
128	33.67	32.37	31.47	30.33
512	54.45	53.13	50.21	49.79
1024	66.25	65.01	62.98	61.90
2048	77.52	73.62	72.06	71.12

Table XVIII.—Dissociation Constants $\times 10^4$

V	0°	15°	25°	35°
32	10.3	10.2	8.7	8.0
128	13.4	13.2	11.3	10.3
512	12.7	13.1	9.9	9.6
1024	12.7	13.5	10.6	9.8
2048	13.1	11.9	11.4	8.4

β-Iodpropionic Acid, CH_2ICH_2COOH

Several recrystallizations were necessary in order to purify this acid, as it decomposes on standing in the presence of light, and the acid as it came from Kahlbaum was found to be quite impure. Its melting point when pure is 85°.

There is also quite a rapid decomposition of the acid when its solution is placed in the cells in the presence of the platinum electrodes, especially at 35°. This made it necessary to refill the cells with fresh solution after the measurements were taken at each temperature.

The decomposition just spoken of may be an explanation of the increase in its temperature coefficients between 25° and 35°, as compared with those from 15°–25°.

Table XIX.—Molecular Conductivity

V	0°	15°	25°	35°
8	6.30	8.42	9.73	11.12
32	12.57	16.81	19.37	21.98
128	23.79	31.86	36.67	41.69
512	44.36	59.47	68.42	78.04
1024	58.61	78.67	91.05	104.24
2048	76.55	102.87	118.35	135.40

Table XX.—Temperature Coefficients

	0°–15°		15°–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	0.141	2.23	0.131	1.56	0.139	1.43
32	0.283	2.25	0.256	1.52	0.261	1.35
128	0.538	2.26	0.482	1.51	0.502	1.37
512	1.007	2.27	0.895	1.51	0.964	1.41
1024	1.337	2.28	1.238	1.57	1.319	1.45
2048	1.755	2.29	1.548	1.51	1.705	1.44

Table XXI.—Percentage Dissociation

V	0°	15°	25°	35°
8	2.836	2.781	2.752	2.744
32	5.657	5.552	5.478	5.425
128	10.71	10.56	10.37	10.29
512	19.97	19.64	19.35	19.26
1024	26.38	25.98	25.75	25.73
2048	34.46	33.98	33.47	33.42

Table XXII.—Dissociation Constants $\times 10^4$

V	0°	15°	25°	35°
8	1.04	1.00	0.97	0.97
32	1.04	1.02	0.99	0.97
128	1.00	0.97	0.94	0.93
512	0.97	0.94	0.91	0.90
1024	0.92	0.89	0.87	0.87
2048	0.89	0.85	0.82	0.82

Levulinic or β-Acetylpropionic Acid, $CH_3CO(CH_2)_2COOH$

The melting point of the acid is 32°.5–33°, so that it was purified by solidifying it, and pressing on a porous plate.

The relation of levulinic acid to those just preceding is brought out by the following tables:

Propionic Acid
White and Jones[1]

V	μ_v 25°	α 25°
8	3.70	1.05
32	7.44	2.10
128	14.57	4.12
512	28.40	8.02
1024	38.94	11.00
2048	53.47	15.10

$K = 0.138$

α-Brompropionic Acid
From Tables XV and XVII

	μ_v 25°	α 25°
	....	...
	58.86	15.38
	114.40	31.47
	186.40	50.21
	229.50	62.98
	262.00	72.06

$K = 10.4$

β-Iodpropionic Acid
From Tables XIX and XXI

V	μ_v 25°	α 25°
8	9.73	2.752
32	19.37	5.478
128	36.67	10.37
512	68.42	19.35
1024	91.05	25.75
2048	118.35	33.47

$K = 0.977$

Levulinic Acid
From Tables XXIII and XXV

	μ_v 25°	α 25°
	4.857	1.39
	9.71	2.79
	19.08	5.48
	36.37	10.44
	49.85	14.31
	66.24	19.02

$K = 0.243$

As we would expect, propionic acid has the lowest values for conductivity, for dissociation and for the constant; and levulinic acid, with an acetyl group in place of one of the hydrogens of propionic acid, has the next higher values. The bromine substitution product is seen to be one hundred times as strong as that containing iodine, which, in turn, is over four times as strong as the acetyl derivative.

Table XXIII.—Molecular Conductivity

V	0°	15°	25°	35°
8	2.939	4.114	4.851	5.539
32	5.85	8.24	9.71	11.10
128	11.57	16.13	19.08	21.84
512	22.06	30.78	36.37	41.68
1024	29.81	41.92	49.85	56.99
2048	39.41	56.31	66.24	76.53

[1] THIS JOURNAL, **44**, 165 (1910).

Table XXIV.—Temperature Coefficients

	0°–15°		15°–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	0.0783	2.66	0.0737	1.79	0.0688	1.42
32	0.160	2.74	0.147	1.78	0.139	1.43
128	0.304	2.63	0.295	1.83	0.276	1.45
512	0.581	2.63	0.559	1.82	0.531	1.46
1024	0.807	2.71	0.793	1.89	0.714	1.43
2048	1.126	2.86	0.993	1.76	1.029	1.55

Table XXV.—Percentage Dissociation

V	0°	15°	25°	35°
8	1.33	1.38	1.39	1.40
32	2.65	2.76	2.79	2.80
128	5.24	5.41	5.48	5.50
512	9.99	10.32	10.44	10.50
1024	13.50	14.06	14.31	14.36
2048	17.84	18.89	19.02	19.28

Table XXVI.—Dissociation Constants $\times 10^4$

V	0°	15°	25°	35°
8	0.224	0.234	0.245	0.249
32	0.225	0.238	0.250	0.252
128	0.226	0.235	0.248	0.250
512	0.217	0.226	0.238	0.241
1024	0.206	0.219	0.233	0.235
2048	0.189	0.209	0.218	0.225

α-Brombutyric Acid, $CH_3CH_2CHBrCOOH$

This acid is very similar in almost every respect to α-brompropionic acid; it is a liquid, boiling at 215°, which was purified by distillation, and was weighed out and made up to proper normality in the usual way. When we compare its conductivity and dissociation with α-brompropionic acid we see that the conductivity, dissociation, and constant of the latter, though somewhat smaller, are yet not very different.

Table XXVII.—Molecular Conductivity

V	0°	15°	25°	35°
32	42.75	54.70	61.0	66.42
128	84.94	109.5	122.8	134.3
512	133.7	173.2	195.2	214.9
1024	160.6	209.3	239.8	266.0
2048	180.7	238.0	275.0	305.9

Table XXVIII.—Temperature Coefficients

	0°–15°		15°–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
32	0.793	1.86	0.630	1.15	0.542	0.889
128	1.64	1.93	1.33	1.21	1.15	0.937
512	2.63	1.97	2.20	1.27	1.97	1.01
1024	3.25	2.02	3.05	1.46	2.62	1.09
2048	3.82	2.11	3.70	1.55	3.09	1.12

Table XXIX.—Percentage Dissociation

V	0°	15°	25°	35°
32	18.53	17.99	17.06	16.30
128	36.82	36.00	34.35	32.97
512	57.97	56.92	54.59	52.74
1024	69.61	68.82	67.08	65.30
2048	78.32	78.26	76.91	75.09

Table XXX.—Dissociation Constants $\times 10^4$

V	0°	15°	25°	35°
32	13.1	13.2	11.0	10.1
128	16.8	17.2	14.0	12.7
512	15.6	16.4	12.8	11.5
1024	15.6	17.0	13.2	12.0
2048	13.8	16.6	12.5	11.1

Hydroxyisobutyric Acid, $(CH_3)_2C(OH)COOH$

Hydroxyisobutyric acid sublimes at 50° and the fresh sublimate melts at 79°.

Ostwald obtained the conductivity of this acid at 25°, and for the sake of comparison his values are given below:

	Ostwald[1]		From Tables XXXI and XXXIII	
V	μ_v 25°	α 25°	μ_v 25°	α 25°
32	20.05	5.65	20.19	5.75
128	38.86	10.95	39.18	11.15
512	73.49	20.70	73.16	20.82
1024	99.52	28.05	97.00	27.61
	$K = 1.06$		$K = 1.06$	

The conductivities agree to within five-tenths of a per cent., except at N/2048. The dissociation given by Ostwald is less

[1] Z. physik. Chem., **3**, 197 (1889).

(except at N/2048), since he used the value $\mu_\infty = 355$, whereas our own value of μ_∞ is 352.6. The mean value for the constant in both cases, however, is the same.

As to the relation of hydroxyisobutyric acid to butyric acid, its constant ($K = 1.06$) is a little less than seven times as great as that of butyric acid ($K = 0.163$). α-Brombutyric acid has a constant ($K = 12.7$), about twelve times as large as the hydroxyl derivative.

Table XXXI.—Molecular Conductivity

V	0°	15°	25°	35°
8	6.075	8.553	10.147	11.576
32	12.11	17.04	20.19	22.97
128	23.50	33.04	39.18	44.65
512	44.06	61.74	73.16	83.41
1024	58.80	81.95	97.00	111.60
2048	76.78	106.95	126.20	144.07

Table XXXII.—Temperature Coefficients

	0°–15°		15°–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	0.165	2.72	0.159	1.86	0.143	1.41
32	0.329	2.71	0.315	1.85	0.278	1.38
128	0.636	2.71	0.614	1.86	0.547	1.40
512	1.18	2.68	1.14	1.85	1.03	1.40
1024	1.54	2.62	1.51	1.84	1.46	1.50
2048	2.01	2.62	1.93	1.80	1.79	1.41

Table XXXIII.—Percentage Dissociation

V	0°	15°	25°	35°
8	2.75	2.838	2.89	2.89
32	5.47	5.653	5.75	5.74
128	10.62	10.96	11.15	11.15
512	19.92	20.48	20.82	20.84
1024	25.58	27.19	27.61	27.88
2048	34.70	35.48	35.92	36.00

Table XXXIV.—Dissociation Constants $\times 10^4$

V	0°	15°	25°	35°
8	0.97	1.05	1.08	1.08
32	0.99	1.06	1.10	1.10
128	0.99	1.17	1.09	1.09
512	0.97	1.03	1.07	1.07
1024	0.94	0.99	1.03	1.08
2048	0.90	0.95	0.98	0.99

Isovaleric Acid, $(CH_3)_2CH.CH_2.COOH$

This acid, boiling at 176°, was fractionally distilled and diluted in the usual manner for nonvolatile liquids. Its relation to the other acids of the aliphatic series is discussed under caprylic acid.

Table XXXV.—Molecular Conductivity

V	0°	15°	25°	35°
8	2.474	3.229	3.666	4.044
32	5.052	6.591	7.493	6.262
128	9.832	12.92	14.69	16.19
512	19.023	24.81	28.13	31.03
1024	26.264	34.22	38.49	42.98
2048	34.804	45.28	51.69	58.02

Table XXXVI.—Temperature Coefficients

	0°–15°		15°–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	0.0503	2.03	0.0473	1.35	0.0378	1.03
32	0.1026	2.04	0.0902	1.36	0.0769	1.03
128	0.2044	2.07	0.1767	1.37	0.1506	1.03
512	0.3856	2.03	0.3318	1.34	0.291	1.03
1024	0.530	2.02	0.427	1.25	0.449	1.16
2048	0.699	2.06	0.640	1.41	0.634	1.22

Table XXXVII.—Percentage Dissociation

V	0°	15°	25°	35°
8	1.15	1.117	1.09	1.06
32	2.35	2.279	2.22	2.16
128	4.59	4.467	4.36	4.22
512	8.86	8.579	8.34	8.10
1024	12.23	11.83	11.42	11.22
2048	16.21	15.66	15.33	15.14

Table XXXVIII.—Dissociation Constants $\times 10^4$

V	0°	15°	25°	35°
8	0.167	0.154	0.150	0.142
32	0.177	0.162	0.158	0.149
128	0.172	0.159	0.155	0.145
512	0.168	0.154	0.148	0.139
1024	0.166	0.151	0.144	0.138
2048	0.153	0.138	0.136	0.132

Caprylic Acid, $CH_3(CH_2)_6COOH$

The easiest method of purifying this acid, which melts at 16.°5, was found to be to solidify it and press out the solid on a porous plate. Being a nonvolatile liquid at ordinary temperatures, solutions of it were made up in a manner similar to that employed for α-brompropionic and α-brombutyric acids.

Table XXXIX.—Molecular Conductivity

V	0°	15°	25°	35°
512	...	...	27.79	31.07
1024	24.39	32.76	37.84	42.35
2048	32.84	44.08	51.08	56.89

Table XL.—Temperature Coefficients

	0°–15°		15°–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
512	...	...	...	...	0.328	1.18
1024	0.558	2.29	0.508	1.55	0.453	1.17
2048	0.749	2.28	0.700	1.58	0.571	1.12

Table XLI.—Percentage Dissociation

V	0°	15°	25°	35°
512	...	...	7.96	7.80
1024	10.84	10.89	10.84	10.64
2048	14.60	14.65	14.63	14.29

Table XLII.—Dissociation Constants $\times 10^4$

V	0°	15°	25°	35°
512	...	...	0.134	0.129
1024	0.129	0.130	0.129	0.124
2048	0.122	0.123	0.123	0.116

We would expect, since caprylic acid is one of the higher aliphatic acids, that its conductivity and dissociation would be less than that of those aliphatic acids with less complex molecules, and such is the case, as was first shown by Ostwald,[1] and as can be seen by comparison of its values with the values in the following tables:

[1] Z. physik. Chem., **3**, 176 (1889).

	Acetic Acid White and Jones[1]		*Propionic Acid* White and Jones		*n-Butyric Acid* White and Jones	
V	μ_V 25°	α 25°	μ_V 25°	α 25°	μ_V 25°	α 25°
512	33.24	9.21	28.40	8.00	29.86	8.44
1024	45.87	12.71	38.94	11.00	41.22	11.64
2048	63.00	17.45	53.47	15.10	59.20	16.15
	$K = 0.175$		$K = 0.133$		$K = 0.163$	

	Valeric Acid Ostwald[2]		*Isovaleric Acid* From Tables XXXV and XXXVII		*Caprylic Acid* From Tables XXXIX and XLI	
V	μ_V 25°	α 25°	μ_V 25°	α 25°	μ_V 25°	α 25°
512	15.7	4.44	28.13	8.34	27.79	7.96
1024	30.4	8.59	38.49	11.42	37.84	10.84
2048	41.9	11.83	51.69	15.33	51.08	14.63
	$K = 0.161$		$K = 0.149$		$K = 0.129$	

l-*Tartaric Acid*, $HOOC(CHOH)_2COOH$

This acid was recrystallized several times from water, and finally dried at 105° in a hot-air bath. The N/8 solution of the pure acid was tested as to its optical activity with a polariscope. The amount of rotation indicated that the acid was pure.

The constant of this acid ($K_{25°} = 10.7$) at 25°, as compared with that obtained by White and Jones for racemic acid ($K_{25°} = 10.8$), indicates a close relationship in chemical activity as well as in structure. Ostwald's values of conductivity, dissociation, etc., of both *d*- and *l*-tartaric acids are given below, and it is seen that though his values of conductivity are not very concordant with our own, the values for the constant are not very different.

	d-*Tartaric Acid* Ostwald			l-*Tartaric Acid* Ostwald		
V	μ_V 25°	α 25°	$K_{25°}$	μ_V 25°	α 25°	$K_{25°}$
32	57.60	16.20	9.8	57.6	16.19	9.7
128	106.2	29.85	9.9	105.6	29.7	9.7
512	184.5	51.80	10.9	183.2	51.5	10.7
1024	236.0	66.0	12.7	234.0	65.8	12.3
2048	291.0	81.8	17.9	289.5	81.4	17.4
	$K = 9.7$			$K = 9.7$		

[1] THIS JOURNAL, **44**, 165 (1910).
[2] Z. physik. Chem., **3**, 175 (1889).

We notice that the constants given by Ostwald increase rapidly with dilution. The same is true of our own, and is no doubt due to the fact that the acid is dibasic and the second hydrogen begins to dissociate at about N/128. Ostwald's figure for the constant, $K_{25°} = 9.7$, includes only the values at N/32 and N/128. If all the values except that at N/2048 are averaged, then his constant would be $K_{25°} = 10.6$, which agrees closely with our own, $K_{25°} = 10.7$, averaged in a similar manner.

Table XLIII.—Molecular Conductivity

V	0°	15°	25°	35°
8	15.64	22.58	26.93	31.12
32	34.18	49.03	58.72	67.65
128	62.81	90.12	107.4	123.5
512	109.3	156.8	186.9	213.0
1024	136.0	192.0	229.4	261.6
2048	171.7	241.0	285.4	325.5

Table XLIV.—Temperature Coefficients

	0°–15°		15°–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	0.463	2.96	0.435	1.93	0.419	1.55
32	0.990	2.94	0.969	1.98	0.893	1.52
128	1.89	3.00	1.73	1.92	3.61	1.47
512	3.17	2.90	3.01	1.92	2.61	1.40
1024	3.73	2.75	3.74	1.95	3.22	1.40
2048	4.62	2.69	4.44	1.84	4.09	1.40

μ_∞ *Values (from graph)*

0°	15°	25°	35°
221.0	298.8	350.0	399.9

$$K_{18°} = [221.0 + (5.28 \times 15) - (0.00486 \times 225)] = 299.1$$

Table XLV.—Percentage Dissociation

V	0°	15°	25°	35°
8	7.08	7.56	7.69	7.78
32	15.47	16.41	16.78	16.91
128	28.42	30.16	30.68	30.88
512	49.46	52.48	53.40	53.25
1024	61.54	64.26	65.54	65.40
2048	77.69	80.66	81.54	81.38

Table XLVI.—Dissociation Constants $\times 10^4$

V	0°	15°	25°	35°
8	6.7	7.7	8.0	8.2
32	8.9	10.1	10.6	10.8
128	8.8	10.2	10.6	10.8
512	9.5	11.3	12.0	11.8
1024	9.6	11.3	12.2	12.1
2048	13.2	16.4	17.6	17.4

Thiodiglycolic Acid, $S(CH_2COOH)_2$

Thiodiglycolic acid ($K_{25}° = 4.8$), as Ostwald[1] showed, is weaker than diglycolic acid ($K_{25}° = 11.0$), the introduction of sulphur in the place of oxygen decreasing the dissociation. Both acids, however, are stronger than either glycolic acid ($K_{25}° = 1.52$) or thioglycolic acid ($K_{25}° = 2.25$), which bear the opposite relation to each other as compared with diglycolic and thiodiglycolic acids.

Ostwald[1] calculated the constants of the latter by a formula somewhat different from that representing the ordinary dilution law:

$$\frac{\alpha^3}{(1-\alpha)V^2} = K$$

From this equation he obtained the value $K_{25}° = 4.8$ for thiodiglycolic acid, whereas we found the value $K_{25}° = 6.51$ for the same acid, calculated by means of the ordinary dilution law. A glance at Table L will show that the constants thus obtained are fairly good up to N/2048, where evidently the second hydrogen begins to dissociate appreciably.

If the above equation is used we obtain the values:

V	$K_{25}°$	V	$K_{25}°$
8	607	512	504
32	257	1024	338
128	113	2048	255

from which it is readily seen that the ordinary law can be better applied to our values.

[1] Z. physik. Chem., **3**, 187 (1889).

Table XLVII.—Molecular Conductivity

V	0°	15°	25°	35°
8	15.70	21.40	25.00	28.16
32	28.86	39.38	46.27	52.18
128	52.79	72.42	84.80	96.00
512	93.31	127.47	148.93	169.03
1024	119.93	164.00	191.30	216.13
2048	152.20	207.38	242.65	275.70

Table XLVIII.—Temperature Coefficients

	0°–15°		15°–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	0.38	2.42	0.36	1.68	0.316	1.26
32	0.70	2.43	0.69	1.75	0.591	1.28
128	1.31	2.48	1.24	1.71	1.12	1.32
512	2.28	2.44	2.15	1.68	2.01	1.35
1024	2.94	2.45	2.73	1.67	2.48	1.30
2048	3.68	2.42	3.53	1.70	3.31	1.36

μ_∞ *Values (from graph)*

V	0°	15°	25°	35°
2048	221.6	300.2	350.1	401.0

$K_t = [221.6 + (532 \times 15) - (0.00544 \times 225)] = 300.2$

Table XLIX.—Percentage Dissociation

V	0°	15°	25°	35°
8	7.09	7.13	7.12	7.02
32	13.03	13.11	13.17	13.01
128	23.83	24.12	24.14	23.94
512	42.12	42.45	42.39	42.15
1024	54.14	34.61	54.46	53.90
2048	68.70	69.06	69.10	68.76

Table L.—Dissociation Constants $\times 10^4$

V	0°	15°	25°	35°
8	6.77	6.85	6.82	6.63
32	6.10	6.18	6.24	6.08
128	5.83	5.99	6.00	5.89
512	5.99	6.11	6.09	6.00
1024	6.24	6.33	6.36	6.16
2048	7.36	7.53	7.54	7.39

Tricarballylic Acid, $HOOC.CH(CH_2COOH)_2$

The acid was recrystallized in the usual manner. It melts at 165°.

Walden[1] and Walker[2] both obtained the conductivity of this acid at 25°. Their values are given in the following tables:

Walden		Walker	
V	μ_v 25°	*V*	μ_v 25°
32	28.33	33.4	29.1
128	54.8	133.6	55.6
512	102.7	534.0	103.0
1024	139.0	1068.0	135.8
$K = 2.2$		$K = 2.24$	

The fact that the constants given in Table LIV agree so well seems to indicate that the acid dissociates all the way up to N/2048 as if it were a monobasic acid.

Table LI.—Molecular Conductivity

V	0°	15°	25°	35°
8	8.26	11.73	14.05	16.24
32	16.39	23.41	28.02	32.38
128	31.82	45.13	53.98	62.28
512	59.35	83.65	99.99	115.38
1024	78.79	110.53	131.67	152.40
2048	103.03	143.90	170.85	196.65

Table LII.—Temperature Coefficients

	0°–15°		15°–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	0.231	2.79	0.231	1.97	0.218	1.55
32	0.468	2.86	0.461	1.97	0.436	1.56
128	0.887	2.79	0.885	1.96	0.830	1.54
512	1.63	2.74	1.63	1.95	1.54	1.54
1024	2.12	2.68	2.11	1.91	2.06	1.57
2048	2.73	2.65	2.70	1.87	2.58	1.51

μ_∞ *Values (determined graphically)*

0°	15°	25°	35°
219.9	296.7	347.6	396.8

$$K_{15} = [219.9 \times (5.22 \times 15) - (0.00438 \times 225)] = 297.2$$

[1] Z. physik. Chem., **10**, 563 (1892).
[2] J. Chem. Soc., **61**, 707 (1892).

Table LIII.—Percentage Dissociation

		15°			
V	0°	from graph	from equation	25°	35°
8	3.76	3.95	3.95	4.04	4.09
32	7.45	7.89	7.88	8.07	8.16
128	14.47	15.21	15.18	15.53	15.69
512	26.99	28.19	28.14	28.77	29.06
1024	35.83	37.25	37.18	37.88	38.39
2048	46.85	48.49	48.41	49.15	49.54

Table LIV.—Dissociation Constants $\times 10^4$

		15°			
V	0°	from graph	from equation	25°	35°
8	1.84	2.03	2.03	2.13	2.18
32	1.87	2.11	2.11	2.21	2.27
128	1.91	2.13	2.12	2.23	2.28
512	1.95	2.16	2.15	2.27	2.33
1024	1.95	2.16	2.15	2.25	2.34
2048	2.02	2.25	2.22	2.32	2.38

p-*Nitrobenzoic Acid*, $O_2NC_6H_4COOH$

The acid was purified by dissolving in alcohol and precipitating by adding a large quantity of water and stirring rapidly. The melting point was found to be 240°.

The constant for *p*-nitrobenzoic acid ($K_{25°} = 4.14$) is much greater, in fact, nearly seven times greater, than that for benzoic acid ($K_{25°} = 0.686$).

Table LV.—Molecular Conductivity

V	0°	12°	25°	35°
512	79.1	104.0	128.9	148.3
1024	99.9	131.5	163.4	187.4
2048	126.8	165.9	205.4	235.4

Table LVI.—Temperature Coefficients

	0°–12°		12°–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
512	2.08	2.63	1.92	1.85	1.95	1.51
1024	2.63	2.63	2.46	1.87	2.40	1.47
2048	3.26	2.57	3.04	1.83	3.00	1.46

Table LVII.—Percentage Dissociation

V	0°	12°	25°	35°
512	35.59	36.55	36.86	37.12
1024	44.93	46.20	46.73	46.86
2048	55.47	58.30	58.73	58.87

Table LVIII.—Dissociation Constants $\times 10^4$

V	0°	12°	25°	35°
512	3.84	4.11	4.30	4.28
1024	3.58	3.87	4.00	4.03
2048	3.43	3.98	4.08	4.11

1,2,4-Dinitrobenzoic Acid, $C_6H_3(NO_2)_2COOH$

The acid was purified by the ordinary method of recrystallization and melted at 179°.

The introduction of two nitro groups into the ortho and meta positions of benzoic acid seems to produce a marked effect on its conductivity, and forms an acid which can be classed among the strong electrolytes. Its constants will be spoken of later in connection with those of the other strong acids.

Table LIX.—Molecular Conductivity

V	0°	15°	25°	35°
32	166.51	212.12	238.54	260.00
128	199.23	262.30	299.83	336.35
512	214.97	288.23	334.50	379.00
1024	218.60	293.40	343.55	391.02
2048	220.00	297.30	347.91	396.83

Table LX.—Temperature Coefficients

	0°–15°		15°–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
32	3.04	1.83	2.64	1.25	2.15	0.90
128	4.21	2.11	3.75	1.43	3.65	1.22
512	4.88	2.27	4.63	1.61	4.55	1.36
1024	5.05	2.31	4.87	1.66	4.80	1.40
2048	5.15	2.34	5.06	1.70	4.89	1.41

μ_∞ *Values (found)*

V	0°	15°	25°	35°
2048	220.00	297.30	347.91	396.83

μ_∞ *Values (calculated from sodium salt)*

V	0°	15°	25°	35°
2048	220.20	297.31	347.97	396.90

Table LXI.—Percentage Dissociation

V	0°	15°	25°	35°
32	75.68	71.34	68.39	65.49
128	90.55	88.21	85.96	84.74
512	97.70	96.93	95.90	95.47
1024	99.35	98.67	98.50	98.49
2048	100.00	100.00	100.00	100.00

1,3,5-Dinitrobenzoic Acid, $C_6H_3(NO_2)_2COOH$

The acid was precipitated from alcoholic solution by means of water. It melted at 205°.

Although the conductivity and dissociation of this acid are fairly high, there is a wide difference between the values for this acid and the corresponding values for the preceding acid. The conductivity and dissociation of the 1,2,4-acid reach a maximum at N/2048, whereas the 1,3,5-acid is only 78.7 per cent. dissociated at the same dilution.

It should be noted that the μ_∞ values of the two acids, however, are practically identical. Moreover, in the case of the 1,2,4-acid, the maximum value of conductivity as measured directly agrees with that obtained from the sodium salt. The fact that the values of the sodium salt prepared by titration agree with those of the salt made up by weight has already been mentioned.

Table LXII.—Molecular Conductivity

V	0°	15°	25°	35°
512	122.28	171.4	203.6	233.5
1024	147.86	205.4	244.0	280.0
2048	167.63	231.9	273.5	313.0

Table LXIII.—Temperature Coefficients

	0°–15°		15°–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
512	3.23	2.64	3.22	1.88	2.99	1.47
1024	3.84	2.60	3.87	1.88	3.59	1.47
2048	4.23	2.52	4.16	1.79	3.95	1.44

Table LXIV.—Percentage Dissociation

V	0°	12°	25°	35°
512	55.52	57.62	58.60	58.83
1024	67.14	69.06	70.23	70.54
2048	76.12	77.96	78.72	78.86

Table LXV.—Dissociation Constants $\times 10^4$

V	0°	15°	25°	35°
512	13.5	15.3	16.2	16.4
1024	13.4	15.1	16.2	16.5
2048	11.9	13.5	14.2	14.4

o-*Chlorbenzoic Acid*, $C_6H_4Cl.COOH$

The acid was purified by the precipitation of the alcoholic solution with water, and was dried in an air bath at 105°. The slightest friction causes the dry acid to become highly charged electrically, so that special precautions must be taken not to agitate it, any more than necessary, before weighing, and it was found best to use a closed bottle for this purpose.

The values found by Ostwald[1] for 25° are given below because they differ quite appreciably from our own at the higher dilutions:

		Ostwald			
V	μ_v 25°	α 25°	*V*	μ_v 25°	α 25°
128	119.4	33.5	512	197.0	55.3
256	156.1	43.8	1024	238.7	67.1

$K = 13.2$

After noticing this disagreement, a second determination was made with a N/512 solution of the acid and a N/2048 solution of the salt at 25°, in order to see whether there had not been some error in making up the first solutions. The following is the result of the second measurement as compared with the first:

		First determination 25°	Second determination 25°
Acid.....	512	194.05	193.82
Sodium salt..	2048	75.47	75.56

The difference in the two determinations of conductivity, both for the acid and the sodium salt, is less than two-tenths of one per cent.

The value of *K* as found by ourselves ($K = 13.6$) is fairly close to that found by Ostwald.

As compared with the nitro substitution product ($K = 4.14$) it is seen from the tables that the chlorine substitution product ($K = 13.6$) has much the larger values both of conductivity

[1] Z. physik. Chem., **3**, 255 (1889).

and dissociation, and the latter has a constant, at 25°, over four times as large as the former.

o-Chlorbenzoic Acid

Table LXVI.—Molecular Conductivity

V	0°	15°	25°	35°
128	85.20	107.08	118.91	128.39
256	109.00	138.40	154.12	167.12
512	134.81	172.70	194.05	211.86
1024	158.72	205.64	232.91	256.43
2048	178.00	233.29	266.52	296.94

Table LXVII.—Temperature Coefficients

	0°–15°		15°–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
128	1.46	1.71	1.18	1.11	0.95	0.80
256	1.96	1.80	1.57	1.14	1.30	0.84
512	2.52	1.87	2.13	1.24	1.78	0.92
1024	3.13	1.97	2.73	1.33	2.35	1.01
2048	3.68	2.07	3.32	1.42	3.04	1.14

Table LXVIII.—Percentage Dissociation

V	0°	15°	25°	35°
128	38.66	35.94	34.12	32.32
256	49.45	46.45	44.22	42.06
512	61.16	57.96	55.67	53.33
1024	72.00	69.01	66.82	64.54
2048	80.76	78.29	76.46	74.74

Table LXIX.—Dissociation Constants $\times 10^4$

V	0°	15°	25°	35°
128	19.0	15.8	13.8	12.1
256	18.9	15.7	13.7	11.9
512	18.8	15.6	13.7	11.9
1024	18.1	15.0	13.1	11.5
2048	16.6	13.8	12.1	10.8

1,2,4-Dihydroxybenzoic Acid, $C_6H_3(OH)_2COOH$

The acid was precipitated from alcohol by water. It decomposed at 213°.

Table LXX.—Molecular Conductivity

V	0°	15°	25°	35°
128	44.74	65.11	79.27	92.14
512	80.73	116.40	140.15	162.02
1024	103.30	147.77	177.20	203.58
2048	127.65	180.58	215.81	248.28

Table LXXI.—Temperature Coefficients

	0°–15°		15°–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
128	1.36	2.04	1.42	2.17	1.28	1.62
512	2.38	2.95	2.38	2.04	2.19	1.56
1024	2.97	2.87	2.94	1.99	2.64	1.46
2048	3.53	2.77	3.52	1.92	3.25	1.50

Table LXXII.—Percentage Dissociation

V	0°	15°	25°	35°
128	20.16	21.71	22.70	23.10
512	36.37	38.82	40.12	40.62
1024	46.54	49.28	50.73	51.04
2048	57.51	60.22	61.79	62.24

Table LXXIII.—Dissociation Constants $\times 10^4$

V	0°	15°	25°	35°
128	3.98	4.62	5.21	5.42
512	4.06	4.81	5.25	5.43
1024	3.94	4.66	5.08	5.12
2048	3.80	4.45	4.88	5.01

1,2,5-Dihydroxybenzoic Acid, $C_6H_3(OH)_2COOH$

The acid was purified like the 1,2,4 compound. It melted at 200°.

It was found to decompose rapidly in the presence of the platinum electrodes, giving a yellow solution; therefore, measurements had to be made as quickly as possible, and a fresh solution had to be introduced into the cells after each reading. This decomposition accounts, no doubt, for the disagreement with Ostwald's values.

Like the two dinitrobenzoic acids given above, these two acids, 1,2,4- and 1,2,5-dihydroxybenzoic acids, have μ_∞ values which agree, though the conductivities and dissociations of the two are quite different. The constants of the 1,2,5-acid ($K_{25°} = 12.8$) are more than twice as great as those of the 1,2,4-acid ($K_{25°} = 5.11$). Ostwald[1] has given a very complete discussion of the relation of the various hydroxybenzoic acids to each other, so that reference only need be made to them here.

[1] Z. physik. Chem., **3**, 247–51 (1889).

Table LXXIV.—Molecular Conductivity

V	0°	15°	25°	35°
128	66.18	95.50	113.96	131.22
512	114.49	163.00	191.90	219.43
1024	141.50	200.68	234.70	267.72
2048	184.36	252.38	290.83	328.42

Table LXXV.—Temperature Coefficients

	0°–15°		15°–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
128	1.95	2.94	1.85	1.93	1.73	1.52
512	3.23	2.83	2.89	1.77	2.75	1.43
1024	3.95	2.79	3.40	1.70	3.30	1.41
2048	4.54	2.46	3.86	1.52	3.76	1.29

Table LXXVI.—Percentage Dissociation

V	0°	15°	25°	35°
128	29.85	31.87	32.49	32.83
512	51.63	54.39	54.71	54.89
1024	63.82	66.97	66.91	66.98
2048	83.15	84.22	82.92	82.17

Table LXXVII.—Dissociation Constants $\times 10^4$

V	0°	15°	25°	35°
128	9.9	11.7	12.2	12.5
512	10.8	12.7	12.9	13.0
1024	10.6	13.3	13.2	13.3
2048	23.9	22.0	19.7	18.5

p-*Sulphamidobenzoic Acid*, $H_2NO_2S.C_6H_4.COOH$

The acid was purified by crystallization. When dry it decomposes at 280°.

We notice here the difference between the amino acids, such as metanilic, sulphanilic, and *o*- and *p*-aminobenzoic acids[1] and the acid amides containing another acid radical. Whereas the temperature coefficients increase with rise in temperature and are very large in the former case, in the latter the temperature coefficients are perfectly normal. The amino group neutralizes the sulpho group but has no effect, practically, on the carboxyl group.

[1] This Journal, **44**, 189 (1910).

The strength of *p*-sulphamidobenzoic acid as compared with that of the amino acids is seen in the following list of constants:

o-Aminobenzoic acid	$K = 0.0671$
p-Aminobenzoic acid	$K = 0.0714$
Metanilic acid	$K = 1.99$
p-Sulphamidobenzoic acid	$K = 2.96$
Sulphanilic acid	$K = 6.55$

Table LXXVIII.—Molecular Conductivity

V	0°	15°	25°	35°
512	67.79	96.00	113.02	128.03
1024	90.60	124.82	146.94	167.17
2048	114.55	157.37	185.11	210.05

Table LXXIX.—Temperature Coefficients

	0°–15°		25°–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
512	1.88	2.77	1.70	1.77	1.50	1.17
1024	2.28	2.52	2.21	1.77	2.02	1.21
2048	2.85	2.49	2.77	1.76	2.49	1.19

μ_∞ *Values*

V	0°	15°	25°	35°
2048	221.70	299.29	349.77	398.0

Table LXXX.—Percentage Dissociation

V	0°	15°	25°	35°
512	30.59	32.06	32.31	32.17
1024	40.88	41.69	42.01	42.01
2048	51.68	52.56	52.92	52.79

Table LXXXI.—Dissociation Constants $\times 10^4$

V	0°	15°	25°	35°
512	2.63	2.96	3.01	2.98
1024	2.76	2.91	2.97	2.97
2048	2.70	2.84	2.91	2.88

Benzenesulphonic Acid, $C_6H_5.SO_3H$

The acid was recrystallized from water, but not dried, since the acid is very hygroscopic. It was standardized in the same way as trichloracetic acid.

It should be noted that the temperature coefficients of strong acids like benzenesulphonic, trichloracetic acids, etc., are much larger than those of the weaker acids, and the increase

in the temperature coefficients with dilution, as well as the decrease with temperature, is very much less rapid.

Table LXXXII.—Molecular Conductivity

V	0°	15°	25°	35°
8	204.57	275.38	321.07	366.1
32	210.23	281.69	326.55	370.1
128	222.14	300.43	350.47	399.8
512	226.92	305.81	356.38	407.0
1024	228.00	308.97	359.03	410.3
2048	226.83	305.71	354.22	407.1

Table LXXXIII.—Temperature Coefficients

	0°–15°		15°–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	4.72	2.31	4.57	1.66	4.50	1.40
32	4.76	2.27	4.49	1.59	4.35	1.33
128	5.22	2.35	5.00	1.67	4.93	1.41
512	5.26	2.32	5.05	1.65	5.06	1.42
1024	5.40	2.37	5.01	1.62	5.13	1.43
2048	5.26	2.32	4.85	1.59	5.29	1.49

μ_∞ *Values*

V	0°	15°	25°	35°
2048	228.00	308.97	359.03	410.3

Table LXXXIV.—Percentage Dissociation

V	0°	15°	25°	35°
8	89.72	89.13	89.43	89.23
32	92.21	91.17	90.95	90.20
128	97.43	97.24	97.62	97.44
512	99.53	98.98	99.26	99.20
1024	100.00	100.00	100.00	100.00

p-*Toluenesulphonic Acid*, $H_3C.C_6H_4.SO_3H$

This acid is similar to benzenesulphonic acid. It has a somewhat lower conductivity, although its percentage dissociation is a little greater (the increase to a maximum, in the case of benzenesulphonic acid, is at a slower rate).

Table LXXXV.—Molecular Conductivity

V	0°	12°	25°	35°
32	203.0	258.5	317.3	361.4
128	208.4	267.0	328.2	374.2
512	210.0	269.0	331.7	376.4
1024	210.6	269.7	332.7	379.3
2048	206.7	266.4	327.7	372.3

Table LXXXVI.—Temperature Coefficients

	0°–12°		12°–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
32	4.62	2.28	4.52	1.75	4.41	1.39
128	4.88	2.34	4.76	1.76	4.60	1.40
512	4.92	2.35	4.82	1.79	4.66	1.41
1024	4.93	2.34	4.84	1.80	4.67	1.40
2048	4.97	2.40	4.76	1.79	4.46	1.36

μ_∞ *Values*

V	0°	12°	25°	35°
2048	210.6	269.7	332.7	379.3

Table LXXXVII.—Percentage Dissociation

V	0°	12°	25°	35°
32	96.40	95.85	95.39	95.30
128	98.97	99.00	98.68	98.68
512	99.72	99.74	99.70	99.26
1024	100.00	100.00	100.00	100.00

m-*Nitrobenzenesulphonic Acid*, $O_2N.C_6H_4.SO_3H$

This acid is similar to the two preceding acids, except that it is not quite so hygroscopic and could be more easily handled. Its conductivity is a little less than that of benzenesulphonic acid, but its dissociation is greater.

Table LXXXVIII.—Molecular Conductivity

V	0°	16°	25°	35°
32	195.9	262.9	307.1	350.0
128	200.5	269.1	313.8	357.2
512	202.0	272.9	320.4	367.2
1024	204.3	275.5	323.5	369.4
2048	204.3	274.6	321.5	368.3

Table LXXXIX.—Temperature Coefficients

	0°–16°		16°–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per. cent.	Cond. units	Per cent.
32	4.47	2.28	4.42	1.68	4.29	1.40
128	4.57	2.28	4.47	1.66	4.34	1.38
512	4.73	2.34	4.75	1.74	4.68	1.46
1024	4.73	2.31	4.20	1.74	4.59	1.42
2048	4.69	2.30	4.69	1.71	4.68	1.45

μ_∞ *Values*

V	0°	16°	25°	35°
1024	204.5	275.5	223.5	369.4

Table XC.—Percentage Dissociation

V	0°	16°	25°	35°
32	95.60	95.43	94.92	94.75
128	97.84	97.68	97.00	96.69
512	98.58	99.09	99.04	99.40
1024	100.00	100.00	100.00	100.00

1,2,4-Nitrotoluenesulphonic Acid, $C_6H_3.CH_3.NO_2.SO_3H$

The acid is very much like the preceding. It is not quite as strong as nitrobenzenesulphonic acid, as would be expected.

Table XCI.—Molecular Conductivity

V	0°	15°	25°	35°
8	176.9	240.9	275.6	312.6
32	193.0	264.1	303.6	344.2
128	198.4	272.0	312.4	354.7
512	199.9	274.3	315.6	358.6
1024	200.5	276.5	318.4	361.9
2048	199.7	274.5	314.8	357.6

Table XCII.—Temperature Coefficients

	0°–15°		15°–25°		25°–35°	
V	Cond. units.	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	4.00	2.26	3.86	1.60	3.70	1.34
32	4.44	2.30	4.31	1.63	4.06	1.34
128	4.60	2.32	4.49	1.65	4.23	1.35
512	4.65	2.33	4.59	1.67	4.30	1.36
1024	4.74	2.37	4.67	1.69	4.35	1.37
2048	4.67	2.34	4.48	1.63	4.28	1.36

μ_∞ *Values*

V	0°	15°	25°	35°
1024	200.5	276.5	318.4	361.9

Table XCIII.—Percentage Dissociation

V	0°	15°	25°	35°
8	88.22	87.12	86.94	86.38
32	96.27	95.52	95.35	95.13
128	98.97	98.37	98.13	98.02
512	99.62	99.22	99.10	99.08
1024	100.00	100.00	100.00	100.00

4,5-Dichlorphthalic Acid, $C_6H_2Cl_2(COOH)_2$

The acid was purified by crystallization from water.

The conductivity of this acid as compared with that of

o-phthalic acid[1] is about 1.5 times as great. This acid evidently dissociates as a dibasic acid, that is, both hydrogens are dissociated, since its conductivity is too great for that of a monobasic acid. One can see from this that it is not possible to find the μ_∞ values of the acid by the graphic method, because this method is applicable only to acids dissociating as monobasic acids.

Nor was it possible to obtain μ_∞ for the sodium salt with the cells we were using. Further work will be carried out later with cells of the cylindrical type on this and the two following acids in order to obtain their μ_∞ values.

Table XCIV.—Molecular Conductivity

V	0°	15°	25°	35°
128	194.24	353.00	286.82	318.34
512	238.55	314.66	359.02	398.42
1024	263.80	348.53	397.13	440.78
2048	288.09	378.49	436.03	487.47

Table XCV.—Temperature Coefficients

	0°–15°		15°–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
128	3.91	2.01	1.38	1.33	3.15	1.10
512	5.07	2.13	4.44	1.41	3.94	1.10
1024	5.65	2.14	4.86	1.39	4.37	1.10
2048	6.03	2.09	5.75	1.52	5.14	1.18

Tetrachlorphthalic Acid, $C_6Cl_4(COOH)_2$

This acid was an exceptionally pure one obtained from Professor W. R. Orndorff and T. G. Delbridge, of Cornell, who had carried out an investigation on its composition and method of purification.[2]

Tetrachlorphthalic acid is quite similar, in general, to dichlorphthalic acid, though its conductivity is much greater.

Table XCVI.—Molecular Conductivity

V	0°	15°	25°	35°
512	296.8	386.5	441.3	492.7
1024	328.6	432.7	495.9	555.2
2048	356.0	469.2	539.8	605.0

[1] This Journal, **44**, 187 (1910).
[2] *Ibid.*, **41**, 393 (1909).

Table XCVII.—Temperature Coefficients

	0°–15°		15°–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
512	5.98	2.02	5.48	1.42	5.14	1.17
1024	6.94	2.11	6.32	1.46	5.93	1.20
2048	7.55	2.12	7.06	1.50	6.52	1.21

Meconic Acid, $(HO)C_5HO_2(COOH)_2 + 3H_2O$

The acid was purified by precipitation from alcohol with water.

Table XCVIII.—Molecular Conductivity

V	0°	15°	25°	35°
32	...	358.6	412.8	146.4
128	347.8	463.2	536.4	598.9
512	412.8	553.6	645.4	729.5
1024	435.9	586.8	686.2	778.0
2048	442.1	597.3	700.1	802.7

Table XCIX.—Temperature Coefficients

	0°–15°		15°–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
32	...	..	5.42	1.58	4.86	1.18
128	7.69	2.21	7.32	1.44	6.25	1.17
512	9.39	2.27	9.18	1.65	8.41	1.33
1024	10.06	2.36	9.94	1.69	9.18	1.34
2048	10.35	2.34	10.28	1.72	10.26	1.47

It is the strongest of all the acids with which we worked. It has the highest percentage temperature coefficients and a conductivity approaching closely to that of sulphuric acid, although it does not give a maximum conductivity.

	Sulphuric Acid Jones and West[1]		*Meconic Acid* From Table XCVIII	
V	μ_V 25°	Cond. units	μ_V 25°	Cond. units
32	491.4	4.22	412.8	4.86
128	589.4	5.68	536.4	6.25
512	675.2	7.78	645.4	8.41
1024	...	...	686.2	9.18
2048	709.9	10.45	700.1	10.26

[1] THIS JOURNAL, **34**, 414 (1905).

Camphoric Acid, $C_{10}H_{16}O_4$

The acid was purified like meconic acid.

It is stronger than the acids of the aliphatic series, but is much weaker than those of the aromatic series. It dissociates, as can be seen from Table CII, like a weak monobasic acid, though it titrates as a dibasic acid.

Table C.—Molecular Conductivity

V	0°	12°	25°	35°
512	24.94	33.05	38.17	42.57
1024	34.05	45.27	52.12	57.99
2048	45.10	59.54	68.15	76.12

Table CI.—Temperature Coefficients

	0°–12°		12°–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
512	0.541	2.17	0.512	1.55	0.440	1.15
1024	0.748	2.20	0.685	1.57	0.587	1.13
2048	0.963	2.14	0.861	1.46	0.797	1.17

μ_∞ *Values (from curve)*

0°	12°	25°	35°
218.3	279.8	344.5	392.5

$$K_{15} = [218.3 + (5.2 \times 12) - (0.00609 \times 144)] = 279.8$$

Table CII.—Percentage Dissociation

V	0°	15°	25°	35°
512	11.43	11.81	11.08	10.85
1024	15.60	16.18	15.13	14.78
2048	20.66	21.28	19.78	19.40

Table CIII.—Dissociation Constants $\times 10^4$

V	0°	15°	25°	35°
512	0.288	0.309	0.270	0.259
1024	0.282	0.305	0.264	0.250
2048	0.263	0.289	0.238	0.228

Uric Acid, $C_5H_4N_4O_3$

The acid was crystallized from water, a small quantity at a time.

Its slight solubility made it impossible to determine its conductivity at any dilution lower than N/2048. It is seen

to be a *very* weak acid, its constant at 25° ($K = 0.0151$) being only about one-fifth that of *p*-aminobenzoic acid ($K = 0.0714$).

Table CIV.—Molecular Conductivity

V	0°	15°	25°	35°
2048	8.34	14.85	18.92	22.77

Table CV.—Temperature Coefficients

	0°–15°		15°–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
2048	0.434	5.20	0.404	2.72	0.385	2.03

μ_∞ *Values (determined graphically)*

V	0°	15°	25°	35°
2048	221.0	298.8	350.0	399.9

$$K_{15} = [221.0 + (5.28 \times 15) - (0.00486 \times 225)] = 299.1$$

Table CVI.—Percentage Dissociation

V	0°	15°	25°	35°
2048	3.77	4.97	5.41	5.71

Table CVII.—Dissociation Constants $\times 10^4$

V	0°	15°	25°	35°
2048	0.0072	0.0127	0.0151	0.0169

Cyanuric Acid, $CO\begin{matrix}\diagup NHCO \diagdown \\ \diagdown NHCO \diagup\end{matrix}NH + 2H_2O$

The acid was purified by recrystallization from water. Its conductivity is so small that it required resistances of over 10,000 ohms to be thrown into the circuit in order to obtain the minimum on the bridge at 35° and measurements at temperatures below this were so inaccurate that they are not given.

Constants could not be obtained with the use of the Ostwald dilution law.

Table CVIII.—Molecular Conductivity

V	35°	*V*	35°
128	1.46	1024	3.52
512	2.78	2048	4.67

Table CIX.—Percentage Dissociation

V	35°	*V*	35°
128	0.360	1024	0.869
512	0.686	2048	1.15

The following acids were tested but were found to be either too insoluble or they decomposed too rapidly:

Thioacetic (decomposed)
Tribromacetic (decomposed)
Phenylbromacetic (decomposed)
Sebacic (insoluble)
p-Brombenzoic (insoluble)
p-Chlorbenzoic (insoluble)
Isophthalic (insoluble)
Brompalmitic (insoluble)
Benzenesulphinic (insoluble)

α-Naphthylaminesulphonic acid and gluconic acid were both tested, but it was found that the solutions had not been standardized properly so they were, for the time being, discarded.

DISCUSSION OF RESULTS

The temperature coefficients of conductivity, expressed in conductivity units, for all the above acids show an increase with dilution of the solution and a decrease with rise in temperature. The rate of increase and decrease is, of course, larger for some acids than for others. The general rule seems to be that the stronger the acid, the less rapid is both the increase with dilution and the decrease with rise in temperature. The very fact that the dissociation of strong acids is so large for all dilutions readily accounts for the small change in the coefficients with dilution.

We know that the temperature coefficients of conductivity for even strong *mineral* acids decrease, to a small extent, with rise in temperature;[1] and also that most of the strong mineral acids are more or less hydrated when in aqueous solution. It is evident that if an acid were not hydrated or only very slightly hydrated (as is the case with most of the weak organic acids), then the decrease in temperature coefficients with rise in temperature would be more rapid, since the complex, hydrated ions could not lose much water, and in consequence, the conductivity could not thus be greatly increased. In order to make this clearer, we have collected in Table CX the values of the temperature coefficients of conductivity for a number

[1] THIS JOURNAL, **34**, 418 (1905).

of weak and practically nonhydrated acids, expressed in conductivity units, for the dilution N/1024 between 0° and 35°.

Table CX.

Acid.	K_0°	0°–15°	15°–25°	25°–35°	Decrease Per cent.
Uric	0.0072	0.43	0.40	0.39	11.6
Caprylic	0.125	0.56	0.51	0.45	19.6
Propionic[1]	0.133	0.61	0.59	0.51	16.4
Acetic[1]	0.175	0.72	0.69	0.62	13.9
Levulinic	0.220	0.81	0.79	0.71	12.4
Camphoric	0.285	0.75	0.69	0.59	21.3

In Table CXI are found the similar values for some of the hydrated acids. There are, in addition to the four strong acids in this table, also two weaker acids—racemic and citric acids—and these show the same decrease in the coefficients as the strong acids.

Table CXI

Acid	Water of cryst. H_2O	0°–15°	15°–25°	25°–35°	Decrease Per cent.
Meconic	3	10.06	9.94	9.18	8.8
Benzenesulphonic	1	5.26	5.05	5.06	3.8
p-Toluenesulphonic	4	4.92	4.84	4.67	5.3
1,2,4-Nitrotoluenesulphonic	2.5	4.74	4.67	4.35	8.2
Racemic,[1] $K_0 = 9.1$	1	3.76	3.56	3.43	8.0
Citric,[1] $K_0 = 6.85$	1	3.64	3.59	3.38	7.1

This indicates that the strength of the acid has very little to do with the gradual decrease in temperature coefficients, but that this decrease is caused by hydration; and the above relation applies to the strong acids only because they are the acids which are most hydrated.

Another interesting point that should be brought out in connection with the temperature coefficients expressed in conductivity units is that the strong acids have the much larger coefficients. This is shown by the following table, which contains the conductivity units of the N/2048 solutions of a number of acids between 0° and 15°, the acids being arranged according to their strength:

[1] White and Jones: THIS JOURNAL, **44**, 159 (1910).

Table CXII

Acid	Cond. units 0°–15°	*K*
Uric	0.434	0.0072
Isovaleric	0.699	0.125
Levulinic	1.13	0.220
β-Iodpropionic	1.76	0.977
p-Sulphamidobenzoic	2.95	2.70
1,2,4-Dihydroxybenzoic	3.53	3.95
α-Brompropionic	3.70	12.4
α-Brombutyric	3.82	14.98
Cyanacetic	4.70	38.7
p-Toluenesulphonic	4.97	(completely dissociated)
Meconic	10.35	

White and Jones found that the percentage temperature coefficients for very nearly all the acids with which they worked showed a slight decrease with increasing dilution, and a much more marked decrease with rise in temperature. We find that the latter decrease is shown by all the acids with which we worked, but there are a number of exceptions to the decrease in temperature coefficients with dilution, probably due to hydrolysis.

All the percentage temperature coefficients of all the acids except uric acid are small, and of the same order of magnitude—not greater than 2.8 per cent. and not less than 2.0 per cent. from 0°–15°—and decrease to 1.7–1.0 per cent. from 25°–35°. That this decrease[1] is regular and of the same order of magnitude throughout would seem to indicate that some constant factor, such as the viscosity of the medium, plays the most important rôle here, and that the viscosity decreases with increasing dilution and rising temperature at the same diminishing rate. That the latter is true is seen from the following data, showing the viscosity of thiodiglycolic acid in aqueous solution:

Table CXIII

	Viscosity at 15°	Viscosity at 25°	Viscosity at 35°
Water[2]	0.01134	0.00891	0.00720
N/2048 solution	...	0.00896	...
N/8 solution	0.01188	0.00927	0.00750

[1] For a full discussion of the decrease in percentage temperature coefficients see Jones and West: THIS JOURNAL, **34**, 418 (1905).

[2] Thorpe and Rogers: Phil. Trans., **185**, 307 (1894); **189**, 71 (1897).

That the conductivity of organic acids is a parabolic function of the temperature was brought out by Schaller and other earlier workers, and by the work of White and Jones, as we have already had occasion to mention in the introduction to this paper. White and Jones plotted several curves, using conductivities as ordinates and temperatures as abscissae, and calculated the conductivity of a number of acids by means of the formula

$$\mu_t = \mu_0 + at - bt^2$$

and found this law to hold in every case.

The curves in Figs. II–V and the values given in Table CXIV are also all in perfect accord with the law, which seems to hold whether the acid is strong or weak, monobasic, dibasic or tribasic. The observed and calculated values in the last two columns of the table are seen to agree very closely.

Table CXIV

	μ_0	a	b	t	Obs.	Calc.
Trichloracetic	221.7	5.24	0.0127	15°	297.6	297.5
α-Brompropionic	124.7	2.84	0.0141	15°	164.1	164.1
β-Iodpropionic	23.79	0.526	0.00040	15°	31.86	31.59
Levulinic	11.57	0.318	0.00070	15°	16.13	16.18
α-Brombutyric	133.7	2.81	0.0140	15°	173.2	172.7
Hydroxyisobutyric	23.50	0.684	0.00229	15°	33.04	33.24
Isovaleric	9.85	0.224	0.00122	15°	12.92	12.94
Thiodiglycolic	93.31	2.37	0.00606	15°	127.47	127.50
Tricarballylic	31.82	0.927	0.00162	15°	45.13	45.36
1,3,5-Dinitrobenzoic	122.3	3.43	0.00750	15°	171.4	172.0
1,2,5-Dihydroxybenzoic	114.5	3.35	0.00983	15°	163.0	162.5
p-Sulphamidobenzoic	90.60	2.41	0.00660	15°	124.8	125.2
Benzenesulphonic	222.1	5.27	0.00563	15°	300.4	300.0
p-Toluenesulphonic	208.4	4.93	0.00549	12°	267.0	266.8
1,2,4-Nitrotoluenesulphonic	198.4	4.79	0.00945	16°	272.0	272.6
Dichlorphthalic	194.2	4.10	0.01576	15°	253.0	252.2

The dissociation of a large number of the acids decreases steadily with rise in temperature. In other cases the percentage dissociation apparently reaches a maximum at some temperature between 15° and 35°, usually around 25°. There are still others whose percentage dissociation increases all

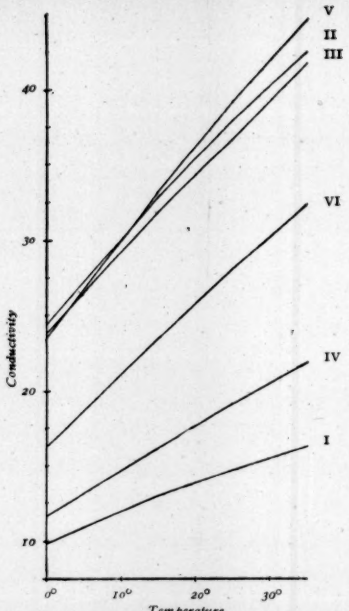

Fig. II—Molecular Conductivity

I. Isovaleric; II. Caprylic; III. β-Iodpropionic; IV. Levulinic; V. Hydroxyisobutyric; VI. Tricarballylic

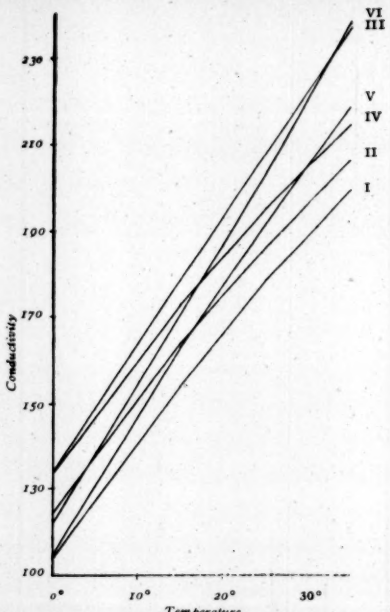

Fig. III—Molecular Conductivity

I. Cyanacetic; II. α-Brombutyric; III. Benzilic; IV. α-Brombutyric; V. 1,2,5-Dihydroxybenzoic; VI. 1,3,5-Dinitrobenzoic

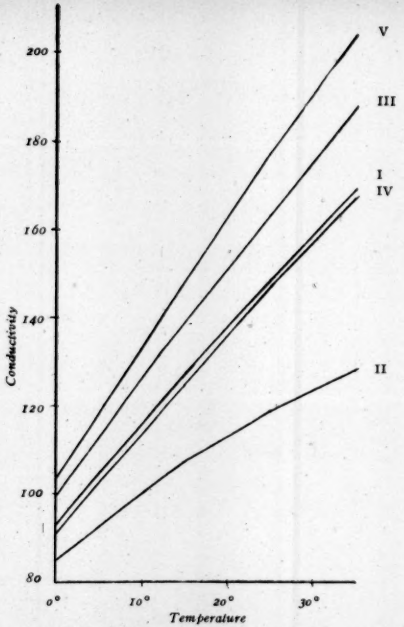

Fig. IV—Molecular Conductivity

I. Thiodiglycolic; II. α-Brompropionic; III. Benzilic; IV. α-Brombutyric V. 1,2,5-Dihydroxybenzoic; VI. 1,3,5-Dinitrobenzoic

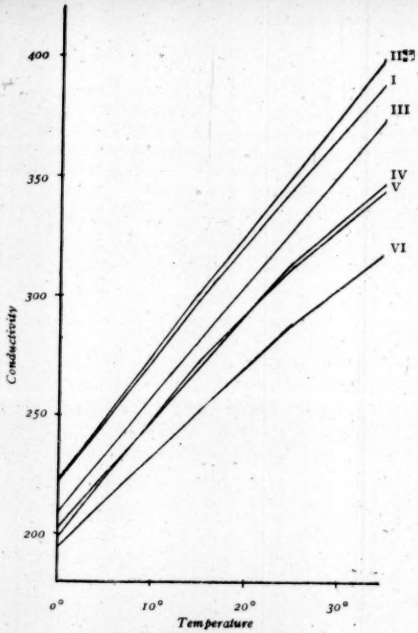

Fig. V—Molecular Conductivity

I. Trichloracetic; II. Benzenesulphonic; III. *p*-Toluenesulphonic; IV. *m*-Nitrobenzenesulphonic; V. 1,2,4-Nitrotoluenesulphonic; VI. Dichlorphthalic

the way up to 35°, though at a diminishing rate. The latter phenomenon is not unusual, Euler,[1] Schaller,[2] and White and Jones,[3] all having observed the same increase in dissociation for more than a dozen acids.

No adequate explanation, however, has been offered, and the problem is a complex one, since there are several factors which can influence the dissociation. Decrease in the association and in the dielectric constant of the solvent with rise in temperature are two well-known causes for the decrease in the dissociating power; and rise in temperature alone, which produces a greater instability in the molecules and a larger ionic mobility, would tend to cause an *increase* in the dissociation. The nature of the dissolved substance itself very likely plays some part, and when all these factors are taken into account, it seems practically impossible to predict beforehand what the result would be.

The following table contains the dissociation constants for all except the strong acids, calculated by means of Ostwald's law:

Table CXV.—Dissociation Constants × 10^4

Acid	0°	15°	25°	35°
Cyanacetic	38.7	37.5	36.3	34.8
Benzilic	9.25	9.15(12°)	9.20	8.93
α-Brompropionic	12.4	12.4	10.4	9.2
β-Iodopropionic	0.977	0.945	0.917	0.910
Levulinic	0.220	0.230	0.243	0.246
α-Brombutyric	14.98	16.1	12.7	11.5
Hydroxyisobutyric	0.96	1.04	1.06	1.07
Isovaleric	0.167	0.153	0.149	0.141
Caprylic	0.125	0.126	0.129	0.123
l-Tartaric	9.45	10.1	10.7	10.7
Thiodiglycolic	6.38	6.50	6.51	6.36
Tricarballylic	1.92	2.14	2.24	2.30
p-Nitrobenzoic	3.62	3.99(12°)	4.14	4.14
1,3,5-Dinitrobenzoic	13.4	15.2	16.2	16.4
o-Chlorbenzoic	13.7	15.5	13.6	11.9
1,2,4-Dihydroxybenzoic	3.95	4.64	5.11	5.25
1,2,5-Dihydroxybenzoic	10.4	12.6	12.8	12.9
p-Sulphamidobenzoic	2.70	2.90	2.96	2.94
Camphoric	0.285	0.307(12°)	0.267	0.254
Uric	0.0072	0.0127	0.0151	0.0169

[1] Z. physik. Chem., **21**, 247 (1896).
[2] *Ibid.*, **25**, 497 (1898).
[3] This Journal, **44**, 196 (1910).

A more general, though empirical, equation for calculating the constants was suggested by Storch,[1] and employed by Bancroft,[2] Noyes,[3] and others, viz.,

$$K = C_i^n / C_s$$

in which $C_i = \frac{\alpha}{V}$ denotes the volume concentration of the dissociated portion, and $C_s = \frac{1 - \alpha}{V}$, the volume concentration of the undissociated part; K and n are both functions of the electrolyte. By using C_i as values along the ordinates and C_s as values along the abscissae, a curve can be plotted from which it is posible to obtain n. The values for n found by previous workers, for a large number of salts and acids, vary from 1.36 to 1.55.

We have attempted by means of this method to obtain constants for the strong acids, but the equation did not seem to be applicable to this case.

Further work on the organic acids, and also on the organic bases, both in aqueous and in nonaqueous solutions, and through a wider range of temperature, is being carried out in this laboratory.

SUMMARY

Several conclusions reached by White and Jones have been confirmed by the present work and are repeated here in quotation marks.

1. The temperature coefficients of conductivity, expressed in conductivity units, increase rapidly with dilution, and decrease rapidly with rise in temperature for weak organic acids—when not hydrated. When the acids are hydrated, the temperature coefficients of conductivity are larger, and their increase with dilution and decrease with rise in temperature both take place at a slower rate.

2. Organic acids with the largest constants also have the largest temperature coefficients of conductivity expressed in conductivity units.

[1] Z. physik. Chem., **19,** 13 (1896).
[2] *Ibid.*, **31,** 188 (1889).
[3] J. Am. Chem. Soc., **28,** 137 (1906); **30,** 333 (1908).

3. "The percentage temperature coefficients of conductivity of the organic acids are generally small and of the same order of magnitude, and decrease with rise in temperature and with increase in dilution."

4. "The conductivity of most of the organic acids is a parabolic function of the temperature, as proved by comparing observed values with those calculated from interpolation formulae."

5. "There is no general statement possible concerning the change in dissociation of the organic acids with change in temperature. Maxima occur with several between 25° and 35°, while in other cases maxima are indicated at slightly higher temperatures than those at which measurements were made. The dissociation of several acids decreases regularly from 0°."

6. The strong organic acids do not obey the Ostwald dilution law, and, therefore, dissociation constants cannot be obtained for them in the ordinary way.

7. The migration velocities of the anions of organic acids are a function of the number of atoms present in the anion, and μ_∞ values for dibasic acids may be found by means of this principle.

8. Most dibasic organic acids dissociate like monobasic acids.

9. "Isomeric acids do not behave similarly as regards change in their dissociation."

10. "The migration velocities of isomeric ions are identical."

11. "The behavior of the organic acids with respect to the change in their dissociation with the temperature is not in accord with the hypothesis of Thomson and Nernst, which connects dissociating power and dielectric constants, or at least the influence of some other unknown force is suggested."

JOHNS HOPKINS UNIVERSITY,
May, 1911

REVIEWS

JAHRBUCH DER CHEMIE. Bericht über die wichtigsten Fortschritte der reinen und angewandten Chemie. Unter Mitwirkung von O. ASCHAN, Helsingfors, H. BECKURTS, Braunschweig, M. DELBRÜCK, Berlin, J. M. EDER, Wien, P. FRIEDLÄNDER, Wien, C. HAEUSSERMANN, Ludwigsburg, A. HERZFELD, Berlin, K. A. HOFMANN, München, G. KEPPELER, Hannover, E. KNECHT, Manchester, J. LEWKOWITSCH, London, A. MORGAN, Hohenheim, B. NEUMANN, Darmstadt, M. NIERENSTEIN, Bristol, P. SACKUR, Breslau, K. SPIRO, Strassburg i. E., herausgegeben von RICHARD MEYER, Braunschweig. XIX Jahrgang. 1909. Braunschweig: Druck und Verlag von Friedrich Vieweg und Sohn. 1910. S. xii + 608.

We take pleasure in welcoming this annual guest, as we have derived much pleasure and profit from such an examination as is possible in the case of a *Jahrbuch*. The preface is a model of brevity and may be quoted in full. It is this: "Diesmal hat weder die Anordnung des Stoffes, noch die Liste der Mitarbeiter eine Änderung erfahren."

This notice might be made equally brief. Thus—the *Jahrbuch* seems to be as good as usual. That would suffice. But we are tempted to refer to a few points that have attracted attention in the perusal. One whose chief interests lie in the field of pure chemistry is more likely to turn to the reports on applied chemistry for in these he is likely to read of things of which his ordinary daily reading has not told him.

New to the writer is the fact recorded under acetylene that this gas is now being used dissolved in acetone under pressures of several atmospheres. This was proposed several years ago but did not at first prove satisfactory. The "acetylen dissous" comes into the market in steel flasks. The pressure employed is 12 atmospheres.

Another interesting fact, new to the writer, but no doubt well-known to the industrial chemist, is that the Sicilian sulphur market is more and more seriously disturbed by American competition. This is true of refined as well as of crude sulphur. Last year an American refinery capable of producing 100,000 tons a year was put up in Marseilles. This quantity is sufficient to meet the demands of the French vineyards. The state of the market is such that, according to the writer in the *Jahrbuch*, "die Bildung eines Schwefeltrusts nur eine Frage der Zeit sei." The American production is increasing slowly: 1902, 7,443 tons; 1903, 35,098 tons; 1904, 193,492 tons; 1905, 215,000 tons; 1906, 294,000 tons; 1907, 307,806 tons; 1908, 312,670 tons.

But let this suffice. Any one interested in the progress of

chemistry will find the *Jahrbuch* full of valuable matter—and most of it *readable*. I. R.

DAS CHEMISCHE GLEICHGEWICHT AUF GRUND MECHANISCHER VORSTELLUNGEN. Von H. v. JÜPTNER, o.ö. Professor an der k. k. technischen Hochschule in Wien. Mit 60 Figuren im Text. Leipzig und Berlin: Druck und Verlag von B. G. Teubner. 1910. S. iv + 367. Preis, geh., M. 11; geb., M. 12.50.

After the great researches upon chemical equilibria at high temperatures carried on some 50 years ago by Henri Sainte Claire-Deville and his followers the attention of physical chemists was diverted into other channels, and it is only within the last ten years that a world-wide interest has been manifested once more in this great problem, the solution of which will permit a deeper insight into the laws, and perhaps the causes, of chemical affinity. On account of the importance of this difficult problem any work which contributes toward an appreciation of the way in which it is being attacked, and of the significant results which have already been obtained, must be most heartily welcomed.

This comprehensive volume of von Jüptner's, containing a large number of numerical tables and other important data, appears on hasty inspection to provide such a résumé of the subject of chemical equilibrium as has long been desired. The reader, however, who examines the work more critically meets only disappointment. The tables which are included in the book have apparently been collected without system, their source is only rarely given, and in many cases they contain old and uncorrected data which have been superseded as the result of more recent investigation. In those cases where the tables have been recalculated, the reviewer has found, even in a hasty inspection, numerous errors or misprints. The book therefore must fail of its purpose, since it is impossible to place reliance upon the figures given, or to trace their source.

Many statements in the work are misleading; for example, that "solubility is in most cases a linear function of the temperature" or that the "dilution law when applied to good electrolytes shows a poorer agreement between calculation and observation than in the case of half-electrolytes, but nevertheless a satisfactory one." In fact, the dilution law predicts the constancy of a certain quantity which in some cases actually changes a millionfold during a hundredfold change in concentration. To regard this as a satisfactory agreement between fact and theory would seem somewhat too complacent.

The author adopts in his theoretical discussion of the sub-

ject the point of view of Nernst, and nearly all of the recent data which are included in the book are those obtained in the important investigations of the Physico-Chemical Institute in Berlin. Thus we find in the index fifty-seven references to the work of Nernst; but only three to Haber, one to Brönsted, and none to Bodenstein.

The first few chapters deal with the laws of gases and with the phenomenon of vapor pressure. Then dissociation of solids, fusion, solution, and the transition from one solid phase to another are successively discussed. Finally gas reactions and the reactions of solutions are considered, and the book ends with some technical applications of the laws of chemical equilibrium to the metallurgy of iron. This forms, indeed, by far the most satisfactory chapter of the book, and will serve well to show to the technical chemist, to whom in part the book is addressed, the numerous ways in which modern physical chemistry may be applied in industrial problems.

GILBERT N. LEWIS.

DAS ACETYLEN, SEINE EIGENSCHAFTEN, SEINE HERSTELLUNG UND VERWENDUNG. Unter Mitwirkung von DR. ANTON LEVY-LUDWIG, Berlin; Dr.-Ing. ARMIN SCHULZE, Berlin; ING. ALFRED SCHNEIDER, Chemnitz; Dr. PAUL WOLFF, Berlin, von PROF. DR. J. H. VOGEL, Berlin. Mit 137 Figuren im Text. Chemische Technologie in Einzeldarstellungen, herausgegeben von FERD. FISCHER. Leipzig: Verlag von Otto Spamer. S. viii + 294. Preis, geh., M. 15; geb., M. 16.50.

One need not read further than the second line to know that this whole series is going to be excellent. The fact that Fischer of the *Jahresbericht* is editor-in-chief is alone sufficient to warrant the purchase of the monographs by every technical school.

The present volumes deal minutely with the physical, chemical and hygienic properties of acetylene, with its analysis and technical preparation. Its various uses and applications as an illuminant, both stationary and portable, as a heating agent for the kitchen and laboratory, for autogenous welding and the cutting of metals and lastly as a raw material from which to make chemical products are carefully and thoroughly discussed. Two chapters on its use in the chemical laboratory and on the laws and official regulations for its handling and use complete this thoroughly satisfactory book.

A valuable feature of the treatise for Americans is the extent to which American work and inventions have been recognized and considered—an encouraging symptom in German writers.

A. H. GILL.

NOTE

INTERNATIONAL ASSOCIATION OF CHEMICAL SOCIETIES

At a meeting of delegates from the Chemical Society of London, the Deutsche Chemische Gesellschaft and the Société Chimique de France, held at Paris April 25–26, an International Association of Chemical Societies was organized with the object of establishing a common bond between the world's chemical societies and of taking up questions of general and international interest in chemistry. Any chemical society is eligible for membership, but only one from each country can be represented in the Governing Council which shall be composed of three delegates from each country. The present Council consists of the delegates from the three founding societies, and representatives of other societies can be admitted to the Council only on a two-third's majority vote of the members voting, votes by correspondence being permitted. The Council shall elect, at the beginning of each meeting, a President who shall take office at the end of the meeting and who, with the other two delegates from his country, acting as Vice-President and General Secretary, respectively, shall constitute an Executive Committee or "Bureau." The functions of the association shall be the appointment of commissions to investigate problems submitted by the Council, the publication of reports in the journals of affiliated societies or in any other form which the Council may select, and the holding of congresses. General expenses shall be borne by the affiliated societies in proportion to the number of their members, but other expenses shall not be assessed against the various societies except on their individual consent. Amendments to the by-laws can be made only on a two-third's majority vote of the Council.

The next meeting will be held in Berlin, April 13, 1912, under the presidency of Prof. Ostwald.